













A TEXT-BOOK OF  
**INORGANIC CHEMISTRY**  
VOLUME V

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# A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.Sc., F.I.C., Ph.D.,

Carnegie Gold Medalist

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**THE PERIODIC TABLE**

PERIODS.	GROUP 0.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.
First short period .	He 4.00	H 1.08 Li 6.94	Gl 9.1	B 11.0	C 12.005	N 14.01	O 16.00	F 19.0	
Second short period .	Ne 20.2	Na 23.00	Mg 24.32	Al 27.1	Si 28.3	P 31.04	S 32.06	Cl 35.46	
First long period { Even series . Odd    "    .	A 39.8 ..	K 39.10 Cu 63.57	Ca 40.07 Zn 65.37	Sc 44.1 Ga 69.9	Ti 48.1 Ge 72.5	V 51.0 As 74.96	Cr 52.0 Se 79.2	Mn 54.93 Br 79.92	Fe Co Ni 55.84 58.97 58.68
Second long period { Even series . Odd    "    .	Kr 83.9 ..	Rb 85.45 Ag 107.88	Sr 87.63 Cd 112.4	Y 88.7 In 114	Zr 90.6 Sn 117	Nb 93.1 Sb 120.2	Mo 95.9 Te 127.5	.. I 126.92	Ru Rh Pd 101.7 102.9 106.7
Third long period { Even series . Odd    "    .	Xe 131.2 ..	Cs 132.81 ..	Ba 137.37 ..	THE RARE EARTH METALS	..	..	..	..	.. .. .
Fourth long period { Even series . Odd    "    .	.. ..	Au 197.2	Hg 200.6	Tl 204.0	Pb 207.20	Ta 181.5 Bi 208.0	W 184.0 ..	.. ..	O Ir Pt 190.9 193.1 195.2
Fifth long period .	Nt 222.4	..	Ra 226.0	..	Th 232.4	..	U 238.2		
Formula of oxides .	..	R <sub>2</sub> O	RO	R <sub>2</sub> O <sub>3</sub>	RO <sub>2</sub>	R <sub>2</sub> O <sub>5</sub>	RO <sub>3</sub>	R <sub>2</sub> O <sub>7</sub>	RO <sub>4</sub>
Formula of hydrides .	..	RH	RH <sub>2</sub>	RH <sub>3</sub>	RH <sub>4</sub>	RH <sub>3</sub>	RH <sub>2</sub>	RH	
Volume in this series of text-books .	1	2	3	4	5	6	7	8	9

The International Atomic Weights for 1917 are adopted in this Table.

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J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.  
CARNEGIE GOLD MEDALLIST

## VOLUME V

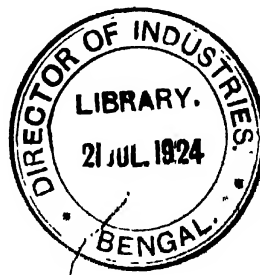
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### CARBON AND ITS ALLIES

BY  
R. M. CAVEN  
D.Sc. (LOND), F.I.C.  
PROFESSOR OF INORGANIC AND ANALYTICAL CHEMISTRY, ROYAL TECHNICAL COLLEGE, GLASGOW

With Frontispiece and 15 Illustrations in the Text

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## GENERAL INTRODUCTION TO THE SERIES

DURING the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned: and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the Elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are sub-



jects of supreme importance to the student of Inorganic Chemistry, and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II, along with the Elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV, along with the Elements of Group III, as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II and V respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II under ammonium, and in Volume IX under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indices and frequent cross-referencing in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen	= 1.00762.	Oxygen	= 16.000.
Sodium	= 22.996.	Sulphur	= 32.065.
Potassium	= 39.100.	Fluorine	= 19.015.
Silver	= 107.880.	Chlorine	= 35.457.
Carbon	= 12.003.	Bromine	= 79.916.
Nitrogen	= 14.008.	Iodine	= 126.920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

## GENERAL INTRODUCTION TO THE SERIES

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Our aim has not been to make the volumes absolutely exhaustive, as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined list.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin and Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND

*October 1917*



## PREFACE

By means of the Periodic System the chemical elements are set in variegated fields, the cultivation of which yields results of high interest and value. A review of each group for the purpose of exhibiting salient characteristics and developing generalisations is an impressive exercise, but one liable to lead to disappointment if simple relations such as those which pertain to members of homologous series of carbon compounds are expected. Anomalies, however, cause questioning and meditation; and thus amidst a bewildering array of chemical facts new relationships are sometimes perceived.

Each of the different groups has an interest of its own; and the fourth group, with which this volume deals, occupies a position of peculiar significance which the Author has sought to point out in the introductory chapter.

Whilst the group contains no element the study of which is quite so fascinating as that of, say, chromium or nitrogen; and, moreover, contains one element, zirconium, about which it would be difficult for any chemist to be enthusiastic; nevertheless some of the elements of the group occupy quite the first rank because of practical importance or theoretical interest.

The group starts with carbon, with its allotropic forms, and coal, the constitution and potentialities of which claim the most serious attention of chemists to-day. Then follow the simple hydrocarbons whose thermal decomposition and combustion have been elucidated by Dixon and Bone, and their co-workers; afterwards comes carbon dioxide, interesting as a gas, and because of its place in nature; and subsequently various other carbon compounds standing on the fringe of the organic field.

Silicon has a double interest: on account of silica, and the natural and artificial silicates, whose constitution, according to the theories of W. and D. Ash and others, is reviewed; and because of the problem of the relation of the element to carbon, to the solution of which the researches of Reynolds, Kipping, and Martin have contributed. The Author is much indebted to Professor Kipping, who kindly criticised the manuscript relating to this subject.

The practical interest in titanium is limited to its use in steel and the employment of the trichloride as a reducing agent; zirconium is noteworthy only because of the difficulty of preparing the metal, and the limited employment of zirconia as a refractory material.

Thorium has assumed great importance in recent years because of the use of thoria in the manufacture of incandescant gas-mantles, and on account of the radioactivity of the element. The Author desires to express his sincere thanks to Mr. H. F. V. Little, B.Sc., Chief Chemist to Messrs. Thorium Limited, and Author of Volume IV in this series,

who read the manuscript and proof of the thorium chapter, and so ensured accurate presentation of a recondite subject.

The very rare element germanium, with which extremely few chemists have any practical acquaintance, is chiefly of note because of the manner of its foretelling and discovery ; but within a limited scope the compounds of this metal show interesting relationships.

The fourth group concludes with the important metals tin and lead. How remarkable it is that these common metals are found in the same periodic field with the scarce germanium ; and how far we are from understanding why some elements are so common and others so rare ! It is hoped that the descriptions of metallurgical and manufacturing processes, and of the properties of the metals themselves, though not exhaustive, will be found clear and adequate.

A valuable source of information and references up to the year 1909 has been Abegg's *Handbuch der anorganischen Chemie*, Band III, 2 ; Thorpe's *Dictionary of Applied Chemistry* has also been consulted, as well as Roscoe and Schorlemmer's treatise.

For more recent work the *Abstracts* and *Annual Reports* of the Chemical Society, and the *Chemisches Zentralblatt*, have supplied references to original papers, and information where the papers were unavailable. Some facts of mineralogy have been gleaned from the *Data of Geochemistry* compiled for the United States Geological Survey by F. W. Clarke.

The Author desires to thank Dr. J. S. Haldane for his original contribution on the physiological action of carbon dioxide, and Mr. F. W. Clifford, the Librarian of the Chemical Society, for revising the list of abbreviations of journals, and for information on some other matters ; and finally, to express his great indebtedness to Dr. J. Newton Friend, the General Editor of this series of text-books, for his invaluable help. Dr. Friend has edited the sections on Atomic Weights, and recalculated the values, and has also read the whole of the manuscript and the proof. On account of these unremitting labours the Author has a degree of confidence in the reliability of the entire work which otherwise he would not possess.

He will nevertheless be grateful for criticisms, and suggestions for improvement.

R. M. CAVEN

UNIVERSITY COLLEGE  
NOTTINGHAM  
October 1917

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## LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

ABBREVIATED TITLE	JOURNAL
<i>Afhandl. Fys. Kem.</i>	Afhandlingar i Fysik, Kemi och Mineralogi
<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Sci.</i>	American Journal of Science
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst
<i>Annalen</i>	Iustus Liebig's Annalen der Chemie
<i>Ann. Chim.</i>	Annales de Chimie (1719-1815, and 1914-)
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie
<i>Ann. Chim. Phys.</i>	Annales de Chimie et de Physique (Paris) (1816-1913)
<i>Ann. Mines</i>	Annales des Mines
<i>Ann. Pharm.</i>	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i>	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i>	Annalen der Physik (1799-1818, and 1900-)
<i>Ann. Physik. Beibl.</i>	Annalen der Physik, Beiblätter
<i>Ann. Sci. Univ. Jassy</i>	Annales scientifiques de l'Université de Jassy
<i>Arbeiten Kaiserl. Gesundheits-amte</i>	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmac.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i>	Archiv der Pharmazie
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles, Genève.
<i>Atti Acc. Torino</i>	Atti della Reale Accademia delle Scienze di Torino
<i>Atti R. Acad. Lincei</i>	Atti della Reale Accademia Lincei.
<i>B. A. Reports</i>	British Association Reports.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i>	See <i>Sitzungsber. K. Akad. Wiss. Berlin</i>
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft
<i>Bot. Zeit.</i>	Botanische Zeitung
<i>Bull. Acad. Sci. Cracov.</i>	Bulletin international de l'Académie des Sciences de Cracovie
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique. Bulletin de la Classe des Sciences
<i>Bull. de Belg.</i>	Bulletin de la Société chimique Belgique.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i>	Bulletin de la Société minéralogique de France
<i>Bull. U. S. Geol. Survey</i>	Bulletins of the United States Geological Survey
<i>Centr. Min.</i>	Zentralblatt für Mineralogie
<i>Chem. Ind.</i>	Die Chemische Industrie
<i>Chem. News</i>	Chemical News
<i>Chem. Weekblad</i>	Chemisch Weekblad
<i>Chem. Zeit.</i>	Chemisches Zentralblatt.
<i>Chem. Zeit.</i>	Chemiker Zeitung (Cöthen)
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris)
<i>Crelle's Annalen</i>	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
<i>Dingl. poly. J.</i>	Düglér's polytechnisches Journal
<i>Drude's Annalen</i>	Annalen der Physik (1900-1906).
<i>Electroch. Met. Ind.</i>	Electrochemical and Metallurgical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Eng. and Min. J.</i>	Engineering and Mining Journal
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Gehlen's Allg. J. Chem.</i>	Allgemeines Journal der Chemie
<i>Gilbert's Annalen</i>	Annalen der Physik (1799-1824) (continued as <i>Pogg. Annalen</i> ).
<i>Giorn. di Scienze Naturali ed Econ.</i>	Giornale di Scienze Naturali ed Economiche
<i>Geol. Mag.</i>	Geological Magazine.
<i>Int. Zeitsch. Metallographie</i>	Internationale Zeitschrift für Metallographie
<i>Jahrb. kl. geol. Reichsanst.</i>	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt
<i>Jahrb. Miner.</i>	Jahrbuch für Mineralogie.
<i>Jahresber.</i>	Jahresbericht über die Fortschritte der Chemie
<i>Jenaische Zeitsch.</i>	Jenaische Zeitschrift für Naturwissenschaft
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society
<i>J. Chem. Soc.</i>	Journal of the Chemical Society
<i>J. Chim. phys.</i>	Journal de Chimie physique
<i>J. Gasbeleuchtung</i>	Journal für Gasbeleuchtung
<i>J. Geology</i>	Journal of Geology.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry
<i>J. Inst. Metals</i>	Journal of the Institute of Metals
<i>J. Miner. Soc.</i>	Mineralogical Magazine and Journal of the Mineralogical Society
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie
<i>J. Physical Chem.</i>	Journal of Physical Chemistry
<i>J. Physique</i>	Journal de Physique
<i>J. prakt. Chem.</i>	Journal für praktische Chemie
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia (Petrograd)
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher
<i>Mém. Paris Acad.</i>	Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut de France.
<i>Mon. scient.</i>	Moniteur scientifique
<i>Monatsh.</i>	Monatshfte für Chemie und verwandte Theile anderer Wissenschaften
<i>Munch. Med. Wochenschr.</i>	Münchener Medizinische Wochenschrift
<i>Nuovo Cim.</i>	Il nuovo Cimento.
<i>Öfvers. K. Vet.-Akad. Förh.</i>	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar
<i>Oesterr. Chem. Zeit.</i>	Oesterreichische Chemiker Zeitung.
<i>Pflüger's Archiv</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentralhalle.
<i>Pharm. Post</i>	Pharmazeutische Post
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh, and Dublin)
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Phys. Review</i>	Physical Review
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift.
<i>Pogg. Annalen</i>	Poggendorff's Annalen der Physik und Chemie (1824-1877) (continued as <i>Wied. Annalen</i> ).
<i>Proc. Chem. Soc.</i>	Proceedings of the Chemical Society
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version)
<i>Proc. Roy. Irish Acad.</i>	Proceedings of the Royal Irish Academy
<i>Proc. Roy. Phil. Soc. Glasgow</i>	Proceedings of the Royal Philosophical Society of Glasgow
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society of London.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh
<i>Rec. Trav. chim.</i>	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
<i>Roy. Inst. Reports</i>	Reports of the Royal Institution
<i>Schweigger's J.</i>	Journal für Chemie und Physik

# LIST OF CHIEF ABBREVIATIONS

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ABBREVIATED TITLE.	JOURNAL.
<i>Sitzungsber. K. Akad. Wiss. Berlin</i>	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. Wiss. Wien</i>	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Wien
<i>Sci. Proc. Roy. Dubl. Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Techn. Jahresber.</i>	Jahresbericht über die Leistungen der Chemischen Technologie.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society
<i>Trans. Chem. Soc.</i>	Transactions of the Chemical Society
<i>Trans. Inst. Min. Eng.</i>	Transactions of the Institution of Mining Engineers
<i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i>	Travaux et Mémoires du Bureau International des Poids et Mesures
<i>Verh. Ges. deut. Naturforsch. Aerzte</i>	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
<i>Wied. Annalen</i>	Wiedemann's Annalen der Physik und Chemie (1877-1899)
<i>Wissenschaftl. Abhandl. phys.-tech. Reichsanst.</i>	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie
<i>Zeitsch. Chem.</i>	Kritische Zeitschrift für Chemie
<i>Zeitsch. Chem. Ind. Kolloide</i>	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift)
<i>Zeitsch. Elektrochem.</i>	Zeitschrift für Elektrochemie
<i>Zeitsch. Kryst. Min.</i>	Zeitschrift für Kristallographie und Mineralogie
<i>Zeitsch. Nahr. Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stochiometrie und Verwandtschaftslehre
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Photochem.</i>	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie



## TABLE OF DATES OF ISSUE OF JOURNALS

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date - a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year	Amer. J. Sci.	Ann. Chem. Phys.	Ann. Min.	Arch. Pharm.	Dongl. J. Pharm.	Collet. Annalen	J. Pharm. Chem.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800		(1) 32-35				4-6		5-8	90	...
1		36-39				7-9		8-11	91	...
2		40-43				10-12		11-14	92	...
3		44-47				13-15		14-17	93	...
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\* First series known as *Bulletin de Pharmacie*.



Year	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. Poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon. Ser.	Phil. Mag.	Phil. Trans.	Phil. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
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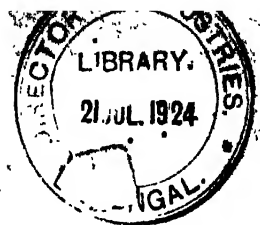
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1915	215, 216		Publication of matter of scientific interest now abandoned.		34		35		54	28	90-93	21	55	89, 90
16	216, 217				35		36		55	29	94-98	22		91, 92
17	217			...	36		37		56	30	99-101	23		93
18	217				37		38		57	31	102-104	24	No issue*	92
19	...				38		39		58	32	105-106	25		92

\* Remainder of vol. 55 appeared in 1920.



# A TEXT BOOK INORGANIC CHEMISTRY.

## VOL. V. CARBON AND ITS ALLIES

### CHAPTER I

#### INTRODUCTORY

##### THE ELEMENTS OF THE FOURTH GROUP CONSIDERED AS A WHOLE

GROUP IV occupies the central position in the periodic system. In Newlands' octaves carbon was preceded by lithium, glucinum, and boron, and followed by nitrogen, oxygen, and fluorine, whilst silicon was preceded by sodium, magnesium, and aluminium, and followed by phosphorus, sulphur, and chlorine.

Series	Group IV	
	A	B
1		...
2		C
3		Si
4	Ti	
5		Ge
6	Zr	
7		Sn
8	..	
9		
10	..	
11		Pb
12	Th	

In Mendeléeff's classification, which extends to elements of higher atomic weight, the same fact is apparent.

For example, in the A' subgroups (see Frontispiece and Chart, p. 2) titanium is preceded by potassium, calcium and scandium, and followed by vanadium, chromium, and manganese, and so on.

This statement is scarcely invalidated by the interpolation of the group of no-valency or noble gases, since these possess no chemical properties, and in the long periods are balanced by the noble metals of Group VIII.

To understand the relationships which subsist between the elements of the fourth group it is necessary first to take a brief survey of the periodic system as a whole, and of the modifications which are found in the relationships of elements in successive groups.

In each series of the periodic scheme the realisable valency of the individual elements rises from 1 in Group I to 7 in Group VII, whilst in physical and chemical properties there is a gradual transition from relatively metallic and electropositive characters to relatively non-metallic and electronegative characters. At the same time there is a



## CARBON AND ITS ALLIES

## THE PERIODIC SYSTEM

(Showing the Disposition of the Fourth Group Elements)

[illegible]

notable distinction between the elements in the short or typical periods and those in the same groups in the long periods: and also between elements analogously situated in the A and B subgroups into which the long periods are divided.

Thus the seven elements of the first short period, from lithium to fluorine, are separated by distinctive properties from all the elements which follow them. For instance, lithium shows exceptional properties when compared with the other alkali metals, and fluorine similarly when compared with the other halogens.

The seven elements of the second short period approximate in properties to the corresponding elements of the long periods: but they are nevertheless, at least in some cases, distinctly separated from them. For instance, whilst sodium stands closer to potassium, rubidium, and caesium than does lithium, it is nevertheless separated from them by the distinctive properties of its salts.

It may be said, therefore, that every element of the first short period is unique by reason of strong individuality, and that the elements of the second short period fail to show such strong individuality, and are more nearly related to the corresponding elements that follow them in the long periods. Thus, for example, chlorine is not separated in properties from the succeeding halogens as fluorine is, and is more closely related to bromine than to fluorine.

In the study of the long periods it is observable in traversing the series of the A subgroups, *i.e.* the even series, that loss of electropositive characters involves approach, not to non-metals, but to the relatively electronegative and inert metals of the eighth group; and that the eighth group characteristics persist in diminishing degree after the odd series of the B subgroups have been entered, but are lost when the second or third group is left behind, and give place at length to electronegative and truly non-metallic characteristics, which culminate in the elements of the halogens.

Thus the series which begins with the powerfully electropositive and metallic element rubidium ends with an unknown element whose place is adjacent to the comparatively inert metals of the eighth group, ruthenium, rhodium, and palladium; whilst the corresponding odd series begins with silver, which is comparatively electronegative, and ends with the halogen element iodine.

When the members of the separate groups which comprise the long periods are considered, it is apparent that as a general rule there is increase of electropositive character or base producing power with rise of atomic weight in a group. Thus, for example, potassium, rubidium, caesium; calcium, strontium, barium; and arsenic, antimony, bismuth, are groups of such elements.

In the eighth group, however, the opposite obtains; there is loss of electropositivity and chemical activity with rise of atomic weight; without, however, the appearance of non-metallic properties. This condition persists in Groups I B and II B; and, according to Abegg,<sup>1</sup> extends to Group III B, but not to Group IV B.

From these considerations it appears that the elements of the A subgroups will be more or less widely separated in properties from the elements of the corresponding B subgroups; and so the question arises as to the relationships of the elements in the short periods to

<sup>1</sup> Abegg, *Zeitsch. anorg. Chem.*, 1904, 39, 367.

those in the subgroups. Thus the elements of the short periods may incline to the corresponding elements of either the A or the B subgroups, or may conceivably be equally related to or separated from both in their properties.

Inspection of the periodic chart shows that the extreme members of the short periods are undoubtedly related to the those of the long periods. For instance, sodium is related to potassium rather than to copper, and chlorine to bromine rather than to manganese.

Moreover, magnesium more closely resembles zinc than calcium, and it appears that after sodium the elements of the second short period are related to the corresponding elements in the B rather than the A subgroups; but that these relationships grow closer as the periods are traversed from magnesium to chlorine and zinc to bromine.

It may further be observed that, whilst the elements of the A subgroups are always more electropositive than the corresponding elements of the B subgroups, the difference in properties between corresponding elements in the A and B subgroups is greatest in the extreme subgroups and diminishes towards the centres of the subperiods K-Mn and Cu-Br. Thus the difference between manganese and bromine is greater than between chromium and selenium, and so on.

These considerations may now be applied in Group IV, first to the relations between carbon and silicon, then to those between silicon and the members of the A and B subgroups, as well as to the relations that corresponding members of the subgroups bear to each other.

**Relation between Carbon and Silicon.**—The unique character possessed by each of the seven elements of the first short period is nowhere more clearly shown than in the case of carbon, which by reason of the enormous number of compounds it forms, and the fact that it enters into the composition of all organic tissues, stands quite alone among the elements.

The fundamental question regarding the relationship between carbon and silicon has to do with the conformation of the atoms of the two elements, or, more strictly, with the space disposition of their valencies. The conception which regards the four valencies of the carbon atom as directed from the centre through the angular points of a regular tetrahedron lies at the foundation of the stereochemistry of carbon, and is plainly capable of extension to other elements of the fourth group.

It has been shown by Kipping,<sup>1</sup> who has prepared "asymmetric" optically active derivatives of  $\text{SiCl}_4$ , that the silicon atom is analogous to that of carbon in the mode of disposition of its valencies. Consequently, in all attempts to represent stereochemically the structure of silicon compounds this tetrahedral form must be taken into account; and in so far as silicon analogues of carbon compounds exhibiting isomerism can be prepared, so far may similar isomerism be expected. For example, if silicon compounds analogous to ethylene derivatives can be prepared, they may be expected to exhibit geometrical isomerism similar to that of fumaric and maleic acids. Likewise, if silicon atoms form ring compounds, either alone or linked through oxygen, in which each silicon atom has two spare valencies which may be satisfied with like or unlike atoms or groups, then it is possible that a kind of isomerism may exist analogous to that exhibited by the substituted polymethylenes.

It is unlikely, however, judging from the analogies suggested by

<sup>1</sup> Kipping, *Trans. Chem. Soc.*, 1907, 91, 209.

## INTRODUCTORY

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the periodic law, that silicon will be found to be very closely related to carbon either in the types of compounds it forms or in the properties of analogous compounds. So far as the evidence goes this view is supported by a comparison of the properties and occurrence of the two elements and their natural compounds, as well as by the differences between the properties of analogous compounds obtained artificially.

Indeed the analogy seems to be restricted entirely to type, for corresponding compounds of a given type are very little alike in properties. Silicenes, for example,  $R_4SiO_4R$ , corresponding in type to ketones, are quite different from them in properties.

Just how far the analogy between carbon and silicon extends, however, has yet to be discovered by the preparation and study of types of silicon compounds beyond those yet known to exist.

An interesting comparison of silicon compounds with corresponding carbon compounds has recently been made by Bygdén, who has measured the refractive indices for the wave lengths of the more important spectral lines of numerous silico-hydrocarbons, and has compared the molecular refractions of these compounds with those of corresponding carbon compounds. It has thus been shown that the replacement of a carbon atom by silicon raises the molecular refraction of the compound by about 5 units (5.00–5.30 for the D line).<sup>1</sup>

**Natural Occurrence of Carbon and Silicon.** Carbon and silicon differ markedly from each other in their mode of natural occurrence. Free carbon is found in various forms in the crust of the earth; silicon has never been found uncombined. Carbon "circulates" between the mineral kingdom and living organisms; silicon does this to only a very limited extent, and probably without reduction from the state of silica. This difference is connected with the superior reducibility of carbon dioxide, as well as with fundamental differences between the two elements as regards the types of compound they can form.

Indeed, silicon appears to enter into the structure of organisms only in the form of derivatives of silicic acid. At least it is quite certain that there is no "organic" chemistry of silicon comparable with that of carbon.

**Allotropy of Carbon and Silicon.** Of the seven pairs of elements constituting the two short periods, carbon and silicon are the only pair which possess comparable allotropic forms.

Indeed the physical properties of these pairs of elements appear to vary in a somewhat irregular manner, except in the first, and perhaps the second, as well as the seventh group. The contrast between boron and aluminum marks a transition from metal to non-metal; that between nitrogen and phosphorus, as well as between oxygen and sulphur, illustrates the wide range of properties between all but the most electronegative non-metals, as compared with the highly electropositive metals (lithium, sodium) on the one hand and the most electronegative non-metals (fluorine, chlorine) on the other.

Thus the recently discovered allotropic nitrogen cannot be put into the same category with the allotropic forms of phosphorus, and allotropic oxygen cannot be compared with allotropic sulphur; but phosphorus and arsenic, and sulphur and selenium, are pairs of elements whose allotropic forms may be compared with those of carbon and silicon.

Although boron has not been mentioned in this comparison because as regards its allotropy it stands alone in the third group, it never-

<sup>1</sup> Bygdén, *Zeitsch. physikal. Chem.*, 1915, 90, 213

theless approaches more nearly to carbon and silicon in physical properties than any other element.

The allotropic forms of carbon and silicon are compared in the following scheme :

**Carbon.**—*Diamond* : Regular Octahedra and Cubes ; Density, 3.519 ; Hardness (on Moh's scale), 10

*Graphite* : Density, 2.06 ; Soft.

*Amorphous* : Density, 1.76.

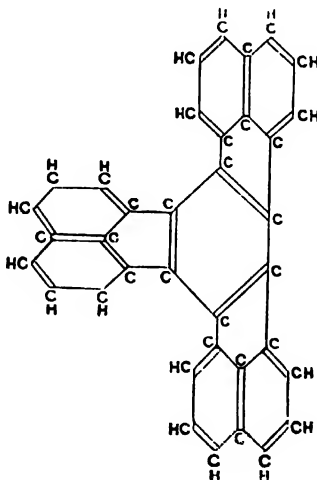
**Silicon.**—*Crystalline* : Regular Octahedra ; Density, 2.49 ; Hardness, 7.

*Amorphous* : Density, 2.35.

Although silicon exists in only two well-defined allotropic forms, while carbon exists in three, there is nevertheless a close resemblance between the physical forms of the two elements.

Thus crystalline silicon is isomorphous with diamond, and even approaches it in hardness, whilst in conducting power for electricity it resembles graphite.

**The Linkage of the Atoms.** A fundamental property of the atoms of carbon, which distinguishes this element from silicon, and indeed from all other elements, is their power of linkage into chains and rings. This is shown primarily in the existence of numerous natural and artificial hydrocarbons whose derivatives constitute the host of compounds of "organic" chemistry. As examples of the extent to which carbon atoms are known to link themselves together, the hydrocarbons dimyrcyl,  $\text{CH}_3(\text{CH}_2)_{58}\text{CH}_3$ , and dekaecylent,  $\text{C}_{36}\text{H}_{72}$  or



may be cited.

Silicon possesses

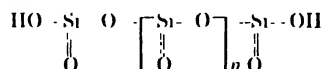
The silicenes  $\text{Si}_2\text{H}_6$ ,  $\text{Si}_3\text{H}_8$ ,  $\text{Si}_4\text{H}_{10}$ ,  $\text{Si}_5\text{H}_{12}$ , and  $\text{Si}_6\text{H}_{14}$  exist,<sup>1</sup> as well

<sup>1</sup> Stoll and Somerski, *Ber.*, 1916, 49, 111

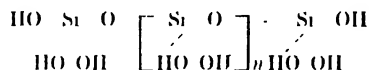
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as the corresponding chlorosilanes  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$ ,  $\text{Si}_4\text{Cl}_{10}$ ,  $\text{Si}_5\text{Cl}_{12}$ , and  $\text{Si}_6\text{Cl}_{14}$ .

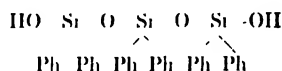
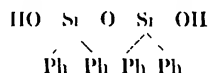
Whether or not the power of linkage of silicon atoms is exhausted in these few compounds, it is certainly very limited compared with that of carbon. Silicon atoms, however, possess to a remarkable degree the power of linkage through oxygen atoms, by reason of which chains, and probably rings, are produced. Thus the natural silicates are derivatives of condensed silicic acids such as:



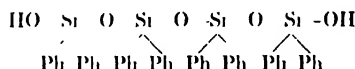
or



to which there correspond, *e.g.* the phenyl derivatives<sup>1</sup>:



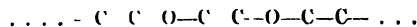
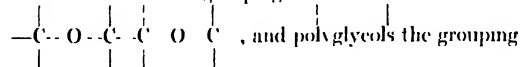
and



The power to form condensed acids, such as the above, in which atoms of the element are linked into a chain through oxygen atoms, is not confined to silicon. It is possessed by boron, as well as by the elements of the sixth group, molybdenum and tungsten especially forming highly complex compounds of this type.

With carbon, however, the power of forming chains with oxygen appears not to be so characteristic. Esters, ethers, anhydrides, and

lactones contain the grouping  $-\text{C}-\text{O}-\text{C}-$ , di-ethers the grouping



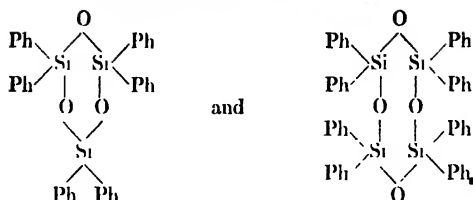
but lengthy chains of alternate carbon and oxygen atoms appear not to exist.

Besides chains, silicon forms rings in which its atoms are alternately linked with oxygen atoms. For example, from the above chain compounds the following rings are derived<sup>2</sup>:

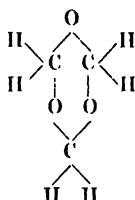
<sup>1</sup> Kipping *Trans. Chem. Soc.*, 1912 101, 2134.

<sup>2</sup> Kipping, *ibid.*

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To the former of these there corresponds the carbon compound trioxymethylene :



Nevertheless it is true to say that the characteristic of carbon is the grouping of its atoms alone into chains and rings, whilst the characteristic of silicon is the formation of chains and rings composed of alternate atoms of silicon and oxygen. The natural hydrocarbons and the natural silicates respectively exemplify these characteristics.

**Analogous Compounds of Carbon and Silicon.**—*Hydrides* The relationship between the hydrides of carbon and silicon is limited to the following compounds :

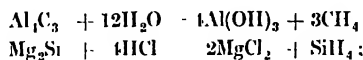
	Carbon		Silicon
Methane	$\text{CH}_4$ , B.P. $-164^\circ \text{C}$ .	Silicane	$\text{SiH}_4$ , B.P. $-112^\circ \text{C}$ .
Ethane	$\text{C}_2\text{H}_6$ .. $-93^\circ \text{C}$ .	Silico-ethane	$\text{Si}_2\text{H}_6$ .. $-15^\circ \text{C}$ .
Propane	$\text{C}_3\text{H}_8$ .. $-44.5^\circ \text{C}$ .	Silico-propane	$\text{Si}_3\text{H}_8$ .. $53^\circ \text{C}$ .
Butane	$\text{C}_4\text{H}_{10}$ .. $-1^\circ \text{C}$ .	Silico-butane	$\text{Si}_4\text{H}_{10}$ .. $0^\circ \text{C}$ . at 7 mm

The boiling-points of  $\text{Si}_3\text{H}_{12}$  and  $\text{Si}_6\text{H}_{14}$  are unknown.

Acetylene,  $\text{C}_2\text{H}_2$ , sublimes  $-83^\circ \text{C}$ . Silico-acetylene  $(\text{Si}_2\text{H}_2)_n$ , solid.

Silico-ethylene,  $\text{Si}_2\text{H}_4$ , and silico-crotonylene,  $(\text{Si}_2\text{H}_4)_2$ , also probably exist.

Hydrosilicons differ widely from hydrocarbons, not only because comparatively few of the former seem capable of existence, but also in chemical as well as physical properties. Methane and silicane resemble one another in their formation by the action of water or acids on metallic carbides and silicides, *e.g.* :



but they differ greatly in their chemical reactions. For instance, silicane is decomposed into its elements at a red heat, but methane may be heated to the melting-point of glass without decomposition.

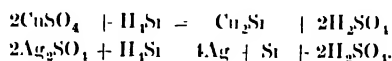
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This difference in stability is quite in accord with what obtains in other groups of the periodic system, in which diminution in stability of gaseous hydrides accompanies rise of atomic weight in the elements; *cf.* for example, ammonia,  $\text{NH}_3$ , with hydrogen phosphide,  $\text{PH}_3$ .

Connected with the relative stabilities of methane and silicane are their relative chemical reactivities.

From copper-sulphate solution silicane precipitates copper silicide, though from the more reducible silver salt the metal separates, together with silicon:



Methane, however, does not react with either of these salts. Phosphine similarly precipitates phosphides from metallic salt solutions, whence ammonia does not precipitate nitrides. Indeed, stability and a kind of chemical inertness corresponding to it are characteristic of the hydrides of the first short period,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{OH}_2$ ,  $\text{FH}$ . The resemblance of silicon to carbon in the remaining hydrides is but slight.

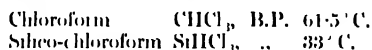
Silico-ethane,  $\text{Si}_2\text{H}_6$ , besides differing from ethane in boiling-point, is decomposed into its elements at  $250^\circ\text{C}$ . and is a vigorous reducing agent, precipitating silver, gold and mercury from their salt solutions, and reacting with sodium hydroxide solution thus:



Ethane is capable of none of these reactions.

Little is known about silico-acetylene except that it is a crystalline solid, which is no doubt polymerised, and as different as possible from acetylene.

*The Chloroforms*—One of the closest resemblances between carbon and silicon is shown by the two compounds:



Both compounds are liquids, and the relation between their boiling-points is similar to that which obtains with the halides, shortly to be noticed. A difference exists between their chemical properties, however, which recalls that between methane and silicane.

Thus silico-chloroform is hydrolysed by water, forming  $\text{SiH}(\text{OH})_3$ , whilst chloroform is quite stable towards water at ordinary temperature; and silico-chloroform yields ethyl orthosilicoformate,  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ , by interaction with alcohol, the corresponding carbon compound only resulting when chloroform reacts with sodium ethoxide.

*The Halides.*—Silicon is more reactive towards the halogens than carbon. Whilst both elements combine directly with fluorine, silicon combines with chlorine at  $450^\circ$  and with bromine at  $500^\circ$ , but not directly with iodine; but carbon unites directly neither with chlorine, bromine, nor iodine.

The halides of silicon, as shown in the following table, have consistently lower boiling-points than those of carbon; and they differ from the latter, like the corresponding hydrides, in their greater reactivity.

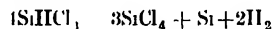


TABLE OF BOILING-POINTS

Fluorides.	Chlorides.	Bromides.	Iodides.
CF <sub>4</sub> —15° C. SiF <sub>4</sub> —90° C.	CCl <sub>4</sub> 76·7° C. SiCl <sub>4</sub> 57° C.	CBr <sub>4</sub> 189·5° C. SiBr <sub>4</sub> 153° C.	CI <sub>4</sub> — SiI <sub>4</sub> c. 290° C.
	C <sub>2</sub> Cl <sub>6</sub> 185·5° C. Si <sub>2</sub> Cl <sub>6</sub> 146–148° C.		
	C <sub>3</sub> Cl <sub>8</sub> 268–269° C. Si <sub>3</sub> Cl <sub>8</sub> 210–215° C.		

Thus silicon tetrachloride, SiCl<sub>4</sub>, is rapidly hydrolysed by water, and so behaves as the chloride of orthosilicic acid; but carbon tetrachloride, CCl<sub>4</sub>, unlike an acid chloride, is quite stable towards water at ordinary temperatures, although it yields carbonate when hydrolysed with alcoholic potash.

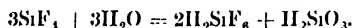
Hexachlor-silico-ethane, Si<sub>2</sub>Cl<sub>6</sub>, is formed by the chlorination of silicon, but at 800° it is decomposed almost completely into silicon and silicon tetrachloride, SiCl<sub>4</sub>. Silico-chloroform, SiHCl<sub>3</sub>, is likewise decomposed by heat as follows:



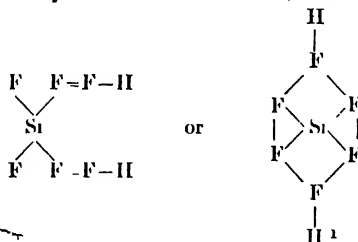
On the other hand, when carbon tetrachloride is passed through a red-hot tube it yields tetrachlorethylene, C<sub>2</sub>Cl<sub>4</sub>, and hexachlorethane, C<sub>2</sub>Cl<sub>6</sub>.

This comparison further illustrates the superior tendency to combine together which carbon atoms possess over those of silicon.

Another striking difference between carbon and silicon is exhibited by their fluorides. Silicon tetrafluoride, SiF<sub>4</sub>, combines with hydrogen fluoride to form hydrofluosilicic acid, H<sub>2</sub>SiF<sub>6</sub>, and also reacts with water thus:



The formation of this complex acid depends upon a special property of the fluorine atom, for there is no chlorine analogue of hydrofluosilicic acid. Probably fluorine is trivalent here, the constitution being



It will, moreover, be an interesting study to compare this acid

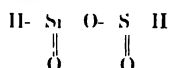
Friend, *The Theory of Valency* (Longmans), 1909.

with analogous complex acids formed by other elements of the fourth group; but it suffices here to point out that carbon forms no corresponding acid,  $\text{H}_2\text{CF}_6$ ; or, in other words, that the carbon atom does not confer on two of the fluorine atoms in carbon tetrafluoride power to combine with molecules of hydrogen fluoride.

*Oxyhalides.*—Carbon forms the oxychloride  $\text{COCl}_2$ , which is the chloride of carbonic acid,  $\text{CO}(\text{OH})_2$ .

Silicon forms no analogous compound, though the oxychloride,  $\text{Si}_2\text{OCl}_6$ , exists, and yields hydrochloric and silicic acids by hydrolysis.

*Oxides and Oxyacids.*—A very important distinction between carbon and silicon is shown in the existence of carbon monoxide, to which silicon seems to furnish no analogue, although the monoxide  $\text{SiO}$  is supposed to be formed in combination when certain silicates are reduced.<sup>1</sup> Carbon monoxide results from the dehydration of formic acid,  $\text{H}\cdot\text{CO}\cdot\text{OH}$ , but silicoformic acid is unknown, though its anhydride,  $\text{H}_2\text{Si}_2\text{O}_3$ , exists, and probably has the constitution

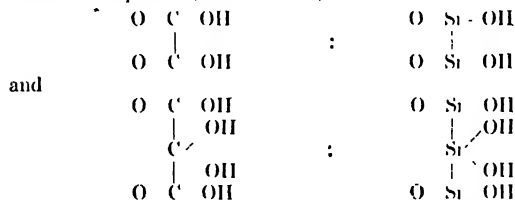


This substance is a strong reducing agent, reacting according to the equation:

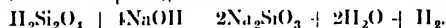


and not thus:  $\text{H}_2\text{Si}_2\text{O}_3 - \text{H}_2\text{O} = 2\text{SiO}$ , which would be the reaction necessary to establish an analogy in this case between carbon and silicon.

Silico-oxalic acid,  $\text{H}_2\text{Si}_2\text{O}_4$ , and silico-mesoxalic acid,  $\text{H}_4\text{Si}_3\text{O}_6$ , derived from their respective chlorides, are analogous in constitution to the corresponding carbon acids, thus:<sup>2</sup>



Silico-oxalic acid differs, however, from oxalic acid by yielding no salts with alkalis, but decomposing thus:



Silico-mesoxalic acid decomposes similarly. These reactions give no sign of the existence of  $\text{SiO}$ .

*The Dioxides.*—There is no more striking difference between carbon and silicon than that between the physical properties of their dioxides. Carbon dioxide is a gas, silicon dioxide a solid fusible only at a very high temperature.

Carbon dioxide shows no tendency to polymerise, silica is a polymer of unknown molecular weight.

<sup>1</sup> Simmonds, *Trans. Chem. Soc.*, 1904, 85, 681.

<sup>2</sup> These acids may, however, have a cyclic constitution, vide Martin, *Trans. Chem. Soc.*, 1915, 107, 310, 1043.

No such extraordinary difference is elsewhere presented between two oxides of the same type.

An important interrelation exists, however, between these two oxides which depends essentially upon this difference in their physical properties. At high temperatures silica displaces carbon dioxide from combination with basic oxides --as, for instance, when silica is fused with sodium carbonate; but at atmospheric temperature, and in presence of water, carbon dioxide displaces silica.

Thus in past ages of the earth's history, when the temperature was high, probably most of the carbon dioxide was in the air, and most of the silica combined with bases in the rocks. The primitive siliceous rocks have, however, been largely disintegrated by atmospheric carbon dioxide, and consequently most of the carbon dioxide in the world is now stored up as carbonates in the sedimentary rocks, whilst much displaced silica exists in the free state.

*Carbonic and Silicic Acids.*—From single molecules of  $\text{CO}_2$  and  $\text{SiO}_2$  ortho and meta acids may be derived thus:



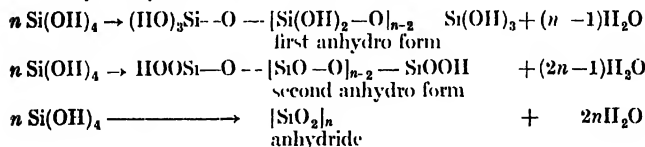
Neither orthocarbonic acid nor its inorganic salts exist, though alkyl orthocarbonates are known, e.g.  $\text{C}(\text{OC}_2\text{H}_5)_4$ . Orthosilicic acid may exist in solution, some of its inorganic salts, such as the magnesium salt  $\text{Mg}_2\text{SiO}_4$ , the chief constituent of olivine, and zircon,  $\text{ZrSiO}_4$ , are known, as well as alkyl salts such as  $\text{Si}(\text{OC}_2\text{H}_5)_4$ .

A solution of carbon dioxide in water contains metacarbonic acid, to which all saline carbonates correspond. Carbonic acid decomposes generating its anhydride with effervescence when it is liberated from its salts; it therefore belongs to the class of unstable acids, which contains sulphurous and nitrous acids.

"Gelatinous silica," dried over sulphuric acid, is approximately represented by the formula  $\text{SiO}(\text{OH})_2$ , though hydrated silica appears always to be of indefinite and variable composition.

Sodium metasilicate,  $\text{Na}_2\text{SiO}_3$ , exists crystallised with various amounts of water; Wollastonite is calcium metasilicate; but most of the natural silicates are derived from condensed silicic acids to which carbonic acid furnishes no analogy whatever.

There is a connection between these condensed acids and polymeric silica, which latter may be regarded as their final dehydration product. This may be represented by the following schemes:



This attempt to express the stages of dehydration of orthosilicic acid must not, however, be taken to mean that highly condensed acids, and silica itself, are necessarily in the form of long chains. More likely they are ring compounds, or may even consist of two or more rings joined together through oxygen atoms.

*Sulphides.*—A comparison of the sulphur compounds of carbon and silicon shows several points of interest.

## INTRODUCTORY

1

Carbon and silicon form the monosulphides CS and SiS. Carbon monosulphide is a non-volatile solid, and therefore a polymer (CS)<sub>n</sub>; silicon monosulphide is volatile. Thiocarbonyl chloride, (CSCl<sub>2</sub>)<sub>2</sub>, is a liquid boiling at 73.5° C.; thioethyl chloride, SiSCl<sub>2</sub>, a crystalline solid melting at 74° C.

Silicon disulphide sublimes at high temperature and is more volatile than the dioxide, whilst carbon disulphide, being a liquid at ordinary temperature, is less volatile than carbon dioxide. Silicon disulphide resembles carbon disulphide in being a thioanhydride, the two sulphides giving rise to thiocarbonates (e.g. Na<sub>2</sub>CS<sub>3</sub>) and thiosilicates (e.g. Na<sub>2</sub>SiS<sub>3</sub>) respectively.

*Compounds with Nitrogen* Whilst nitrogenous carbon compounds are exceedingly numerous and important, corresponding compounds of silicon are few, and those that exist bear little resemblance to their carbon analogues.

The compound SiNH does not resemble hydrocyanic acid, HCN; silicothionica, SiS(NH<sub>2</sub>)<sub>2</sub>, differs from its carbon analogue in being decomposed by water: the amino grouping  $\text{>Si-NH}_2$  shows no rela-

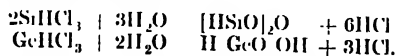
tionship to the corresponding carbon grouping  $\text{>C-NH}_2$ . Nevertheless the anhydride Si(NHC<sub>6</sub>H<sub>5</sub>)<sub>4</sub> does resemble in behaviour the corresponding carbon compound.

**Comparison of the Elements of the A and B subgroups with Carbon and Silicon.** It has already been suggested in the introductory study of the fourth group that the elements of the B subgroup will be rather more closely related to carbon and silicon than those of the A subgroup, being therefore somewhat more electronegative than the latter; but that the difference in properties between similarly situated elements in the two subgroups will be less pronounced than in any other group of the periodic system. These two points may now be elucidated by comparing silicon with germanium and titanium respectively.

Silicane, SiH<sub>4</sub>, is rather unstable; nevertheless the close relationship between germanium and silicon is shown by the existence of an unstable hydride, GeH<sub>4</sub>, and by the two chloroforms

SiHCl<sub>3</sub> B.P. 34° C.; GeHCl<sub>3</sub>; B.P. 72° C.,

which, however, are differently decomposed by water, because germanium forms no condensed acid:



Whether or not titanium can form a gaseous hydride, TiH<sub>4</sub>, or a chloroform, TiHCl<sub>3</sub>, is an interesting question. It has not been found possible to prepare TiHCl<sub>3</sub>,<sup>1</sup> but there is some evidence of the possible existence of TiH<sub>4</sub>.<sup>2</sup> Undoubtedly, however, germanium forms a more stable volatile hydride and chloroform than titanium.

Alkyls, both of metals and non-metals, are more stable than the corresponding hydrides. Germanium alkyls exist, but it is doubtful if titanium alkyls have been obtained. If they existed they would

<sup>1</sup> Schneider, *Zeitsch. anorg. Chem.* 1895, 8, 81

<sup>2</sup> Renz, *Ber.*, 1906, 39, 240

## CARBON AND ITS ALLIES

constitute an exception to the rule that organo-metallic compounds are confined to metals in the B subgroups of the periodic system.

Titanium tetrachloride,  $\text{TiCl}_4$ , boils at  $136^\circ \text{C}$ ; germanium tetrachloride,  $\text{GeCl}_4$ , notwithstanding the higher atomic weight of germanium, boils at  $86^\circ \text{C}$ .

Titanium dioxide,  $\text{TiO}_2$ , forms the disulphate  $\text{Ti}(\text{SO}_4)_2$ ; germanium dioxide,  $\text{GeO}_2$ , forms no oxysalts.

These facts suffice to show that titanium is somewhat more metallic, and therefore less closely related to silicon than is germanium, though the contrast between the two elements is not great.

What is true of these two elements is true of the series of elements of which they are the first members, so that the elements zirconium, cerium, and thorium are more distinctly metallic than the elements tin and lead.

It now remains to study the gradation of properties of the elements of Group IV B, namely, germanium, tin, and lead, which closely follow carbon and silicon; then to make a similar study of the Group IV A elements, namely, titanium, zirconium, cerium, and thorium; and finally, by means of the facts adduced, to institute a general comparison between the two subgroups.

## COMPARATIVE STUDY OF GERMANIUM, TIN, AND LEAD

**The Metals.** The gradation of properties presented by these three metals is set forth in the accompanying table. According to the interpretation of the periodic system already given, this gradation should show an increase in metallic properties with rise of atomic weight. In a general way this is the case; though, as will be seen, not all the properties of the metals point to this conclusion.

## COMPARATIVE STUDY OF GERMANIUM, TIN, AND LEAD

	Ge	Sn	Pb
Atomic weight	72.5	118.7	207.20
Physical characters	Greyish white, lustreous, brittle	White, highly lustreous, ductile, not tenacious, malleability diminishes with rising temperature, brittle at $200^\circ \text{C}$	Bluish-grey, soft, tough, malleable
Crystalline form	Crystallises in regular system	Tetragonal	Regular octahedra and monoclinic plates
Density	5.47	7.30	11.35
Atomic heat	About 5.5	6.2	6.2
Melting-point	$958^\circ \text{C}$	$231^\circ \text{C}$	$327^\circ \text{C}$
Boiling-point	Above $1350^\circ \text{C}$	Very high	$1140^\circ$ $1142^\circ \text{C}$
Allotropic forms	None known	Grey tin, stable below $20^\circ$ , density 5.8; Rhombic tin, density 6.5	None definitely known
Action of air	None	None	Film of $\text{Pb}_2\text{O}$ formed
Action of $\text{HCl}$	None	$\text{SnCl}_2 + \text{H}_2$	$\text{PbCl}_2 + \text{H}_2$
Action of $\text{HNO}_3$	Forms $\text{GeO}_2$	Dilute yields $\text{Sn}(\text{NO}_3)_4$	$\text{Pb}(\text{NO}_3)_2$
		Concentrated yields hydrated $\text{SnO}_2$	

The question of allotropy is of interest here. Tin exists in three allotropic forms. Lead, being more metallic than tin, does not exhibit such well-defined allotropy; but germanium might be expected to show this phenomenon clearly, especially as it approximates to silicon in other properties. That no allotropy has been observed may perhaps be attributed to the rarity of germanium.

The melting-point of germanium is much higher than that of tin or lead; but in this it approximates to silicon, which also it resembles in the value of its atomic heat (At. Ht. Si = 5.7); whilst the atomic heats of tin and lead show the normal value for metals.

Conductivities for heat and electricity do not follow the periodic law; but the action of acids on these three metals is significant.

No element less electropositive than hydrogen displaces this element from hydrochloric acid. Germanium has no action on this acid, being in all probability less electropositive than hydrogen. Tin and lead both displace hydrogen slowly from the concentrated acid, and lie close together in the electropotential series immediately above hydrogen. Indeed it cannot certainly be affirmed that lead is more electropositive than tin. Possibly the influence of the relationship as regards electropotential which obtains in the eighth group extends even as far as Group IV B.

The reactions of these metals towards nitric acid bear a different significance, for they involve the question of the existence of oxy-salts. Germanium, which forms the dioxide without the intermediate appearance of nitrate, is more reactive than silicon, which is inert towards nitric acid alone; but tin forms in solution unstable stannous nitrate with the dilute acid, and with more concentrated acid a still less stable stannic nitrate which quickly passes into hydrated stannic oxide, or metastannic acid. Lead, however, forms the stable nitrate  $\text{Pb}(\text{NO}_3)_2$ , which is not much hydrolysed by water. Thus is shown an emphatic chemical difference between tin and lead, to which there is no corresponding electropotential difference; this is one amongst other examples which indicate that the basic and electrochemical properties of the elements in a natural group may not stand in the same relation.

**Valency.**—Each of these elements manifests the typical group valency of four, and it has been shown in the case of tin<sup>1</sup> that the disposition of these valencies conforms to the tetrahedral type characteristic of carbon, since "asymmetric" optically active derivatives have been prepared. Besides being quadrivalent, each element forms a series of compounds in which it is bivalent. As in the fifth group, the elements of lower atomic weight tend to form compounds in which the higher valency is satisfied, whilst as regards the elements of higher atomic weight the compounds where the lower valency is exercised are the more stable. Thus the germanous ion  $\text{Ge}^{++}$  reduces  $\text{CrO}_4^{--}$ ,  $\text{MnO}_4^{--}$ , and  $\text{Au}^{+++}$  to  $\text{Cr}^{+++}$ ,  $\text{Mn}^{++}$  and gold respectively; the stannous ion,  $\text{Sn}^{++}$ , reduces  $\text{Hg}^{++}$  to  $\text{Hg}$  and mercury,  $\text{Fe}^{++}$  to  $\text{Fe}$  and  $\text{Cu}^{++}$  to  $\text{Cu}$ ; whilst the lead ion  $\text{Pb}^{++}$  has no reducing properties whatever. On the other hand, quadrivalent lead compounds are oxidising agents, being reduced in presence of acid to salts of  $\text{Pb}^{++}$ . Further, the tetrachlorides of germanium and tin are liquids which distil unchanged; whilst lead tetrachloride,  $\text{PbCl}_4$ , cannot be distilled, but decomposes at atmospheric temperature into  $\text{PbCl}_2 + \text{Cl}_2$ .

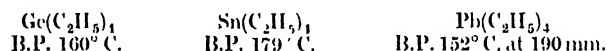
<sup>1</sup> Pope and Peachey, *Proc. Chem. Soc.*, 1900, 10, 42, 115.

It is to be observed, moreover, that none of these elements exhibits tervalency. In this respect they differ in a noteworthy manner from the elements of the A subgroup (*q.v.*).

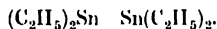
**Atomic Linkage.**—It was seen that silicon falls far short of carbon in its power of atomic linkage; and germanium, tin, and lead resemble the majority of elements in not forming compounds containing chains of their atoms. Stannous chloride vapour may, however, contain the molecules  $\text{Cl}_2\text{Sn}-\text{SnCl}_2$ , thus resembling ferrous chloride, whose vapour at low temperatures contains  $\text{Fe}_2\text{Cl}_4$  molecules.

Tin appears to resemble silicon, however, in forming chains, or perhaps rings with alternate oxygen atoms; these probably exist in  $\beta$ -metastannic acid and its derivatives, which are known to be polymeric.

**Hydrides and "Organo-metallic" Compounds.**—The power to form a volatile hydride,  $\text{MH}_4$ , is limited to germanium, but, in accordance with a well-known principle, the power to form volatile organo-metallic compounds may be expected to extend to elements of higher atomic weight. As a matter of fact tin and lead, as well as germanium, form these compounds, in which the metal is quadrivalent, thus:



Tin also forms a diethyl, which is supposed to be  $\text{Sn}(\text{C}_2\text{H}_5)_2$ , in which the metal is bivalent; but this compound may be of the ethylene type:



**Halides.**—The following halides are typical:

	Ge	Sn	Pb
$\text{MCl}_2$	$\text{GeCl}_2$ , colourless fuming liquid, reducing agent, hydrolysed by water to $\text{Ge}(\text{OH})_2$	$\text{SnCl}_2$ , prisms, M.P. $250^\circ \text{C}$ , B.P. $606^\circ \text{C}$ . Moderately sol. in ether. Strong reducing agent, hydrolysed by much water to $\text{Sn} < \text{OH}$	$\text{PbCl}_2$ , M.P. about $500^\circ \text{C}$ , B.P. $956^\circ \text{C}$ . Insol. in ether, not a reducing agent, not hydrolysed by water
$\text{MCl}_4$	$\text{GeCl}_4$ , liquid, B.P. $86^\circ \text{C}$ , slowly hydrolysed to $\text{GeO}_2$	$\text{SnCl}_4$ , liquid, B.P. $113.9^\circ \text{C}$ , forms hydrates with cold water, hydrolysed by much water	$\text{PbCl}_4$ , yellow liquid, decomposes easily to $\text{PbCl}_2 + \text{Cl}_2$ , explosively at $105^\circ \text{C}$ , forms hydrate with a little water; hydrolysed by excess
Complex halides	$\text{H}_2\text{GeF}_6$ and salts	$\text{H}_2\text{SnF}_6$ (?) $\text{K}_2\text{SnCl}_6$ , $\text{K}_2\text{SnCl}_4$ $\text{K}_2\text{SnF}_6$ , $\text{K}_2\text{SnCl}_6$	$\text{K}_2\text{PbCl}_4$ , etc. $\text{K}_2\text{HPbF}_6$ $\text{K}_2\text{PbCl}_6$

If it is remembered that a non-metallic chloride is usually distinguished from a metallic chloride by volatility, solubility in non-hydroxylic solvents (*e.g.* ether), and by being hydrolysed by water, it will be seen that the above dichlorides illustrate a transition from almost non-

metallic characters in germanium to almost metallic characters in lead. At the same time, the fact that lead dichloride,  $\text{PbCl}_2$ , is not a reducing agent shows that lead does not assume the quadrivalent form so readily as tin or germanium. The tetrachlorides approach more nearly to the properties of non-metallic chlorides than the dichlorides, but those of tin and lead are shown to possess some saline characters by forming crystalline hydrates; while the instability of lead tetrachloride,  $\text{PbCl}_4$ , might be expected from the non-reducing property of the dichloride just referred to.

The complex halides are instructive. The formation of a double or complex salt always depends upon the existence of some electrochemical difference between its component salts, though the difference between a double and a complex salt is only one of degree. It may well be supposed that all the halides under consideration are sufficiently electronegative or non-metallic in character to combine with alkali halides, and many of them do so combine.

It appears singular, however, that in the case of germanium only the complex fluoride is known. It is noteworthy that in this respect germanium is quite analogous to silicon, which forms the complex acid  $\text{H}_2\text{SiF}_6$ , but no other complex halogen acid.

**Oxides, Hydroxides, and Salts.** All three elements form mono- and di-oxides to which certain hydroxides and oxysalts correspond, thus:

GeO	SnO	PbO
$\text{Ge(OH)}_2$	$[\text{Sn(OH)}_2 \text{ unknown}]$	$[\text{Pb(OH)}_2 \text{ unknown}]$
$\text{H} \cdot \text{GeO} \cdot \text{OH}$	$2\text{SnO} \cdot \text{H}_2\text{O}$ $\text{HSnO} \cdot \text{ONa}$	$2\text{PbO} \cdot \text{H}_2\text{O}$ , $3\text{PbO} \cdot \text{H}_2\text{O}$ $\text{HPbO} \cdot \text{ONa}$
No oxysalts	$\text{SnSO}_3$ $\text{Sn(NO}_3)_2$	$\text{PbSO}_3$ $\text{Pb(NO}_3)_2$ , $\text{PbCO}_3$ , etc.
$\text{GeO}_2$	$\text{SnO}_2$	$\text{PbO}_2$
$\text{Ge(OH)}_4$ , $\text{GeO(OH)}_2$ (?) (fictitiously acidic, and basic)	$\text{H}_2\text{SnO}_3$ $(\text{H}_2\text{SnO}_3)_2$ or $\text{H}_2\text{Sn}_3\text{O}_{11} \cdot 11\text{H}_2\text{O}$ and $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 2\text{H}_2\text{O}$  $\text{Sn(OH)}_4$  $\text{Sn(SO}_3)_2$ $[\text{Sn(NO}_3)_4]$	$\text{H}_2\text{PbO}_3$ $[\text{Pb(OH)}_4 \text{ unknown}]$ $\text{Pb}_2\text{O}_3$ , $\text{PbPbO}_3$ $\text{Pb}_3\text{O}_4$ , $\text{Pb}_2\text{PbO}_4$ $\text{Ca}_2\text{PbO}_4$ $\text{CaPbO}_3$ also $\text{H}_2\text{Pb}_2(\text{OH})_6$ $\text{K}_2\text{Pb}_2(\text{OH})_6$ $\text{Pb(SO}_4)_2$ $\text{Pb(C}_2\text{H}_3\text{O}_2)_4$ , etc.

That the monoxides increase in basic power from germanium to lead can be judged from a consideration of the oxysalts. Germanium monoxide forms no oxysalts; stannous sulphate and nitrate exist, but there is no carbonate; lead monoxide forms numerous oxysalts, including a carbonate, and is thereby shown to be a basic oxide of considerable power. That the hydrated oxides diminish in acidic power from germanium to lead has been shown by Hantzsch,<sup>1</sup> who has proved

<sup>1</sup> Hantzsch, *Zeitsch anorg Chem*, 1902, 30, 289



progressive hydrolysis of the sodium salt solutions :  $\text{HGeO} \cdot \text{ONa}$ ,  $\text{HSnO} \cdot \text{ONa}$ ,  $\text{HPbO} \cdot \text{ONa}$ .

Germanic oxide,  $\text{GeO}_2$ , is soluble in acids and alkalis, in which it exists as the cation  $\text{Ge}^{++}$  and the anion  $\text{GeO}_3^{--}$  respectively. No salts, however, have been isolated from these solutions, but from its solution in alkali carbon dioxide precipitates germanic oxide,  $\text{GeO}_2$ .

Considering how closely germanium resembles silicon in the compounds  $\text{GeH}_4$ ,  $\text{GeHCl}_3$ ,  $\text{GeCl}_4$ , it is singular that there should appear little resemblance between germanic oxide and silica.

Stannic oxide,  $\text{SnO}_2$ , differs from germanic oxide,  $\text{GeO}_2$ , in forming condensed acids containing five atoms of tin, which recall the complex silicic acids, and also by exhibiting feebly basic properties in the sulphate  $\text{Sn}(\text{SO}_4)_2$ , and an unstable nitrate,  $\text{Sn}(\text{NO}_3)_4$ .

Lead dioxide,  $\text{PbO}_2$ , differs from stannic oxide,  $\text{SnO}_2$ , in the types of acid to which it gives rise, since ortho and meta plumbates are known, as well as salts of the acid  $\text{H}_2\text{Pb}(\text{OH})_6$ ; but lead forms no condensed acids analogous to those of tin. Lead dioxide also differs from stannic oxide in forming salts with the lower oxide  $\text{PbO}$ ; since  $\text{Pb}_2\text{O}_3$  is lead metaphosphate,  $\text{Pb}_2\text{PbO}_4$ , and  $\text{Pb}_3\text{O}_4$  lead orthophosphate,  $\text{Pb}_2\text{PbO}_4$ . Probably, however, this difference should be attributed to the superior basic power of litharge over stannous oxide, rather than to acidic difference between plumbic and stannic oxides. There are no exact data to show that lead dioxide is a weaker acidic oxide than stannic oxide, but the following difference in behaviour is noteworthy.

When bromine-water is added to the solution obtained by adding excess of alkali hydroxide to stannous chloride solution, alkali stannate is formed; but when a similar experiment is performed with a lead solution, hydrated lead dioxide is precipitated. This result suggests that lead dioxide is less acidic than stannic oxide; and that the former is the more basic is shown by the existence of various salts of quadrivalent lead such as the sulphate, acetate, etc.

**Sulphides.** The properties of the sulphides accentuate the chemical difference between tin and lead more than those of the oxides. Sulphides are naturally less acidic than the corresponding oxides, and precipitated lead sulphide, unlike hydrated litharge, is insoluble in alkali hydroxide solution, in which stannous sulphide,  $\text{SnS}$ , being more acidic than lead sulphide,  $\text{PbS}$ , dissolves somewhat tardily.

Lead is not known to form a disulphide, a fact which emphasises the inferior stability of quadrivalent lead compounds; but stannic sulphide,  $\text{SnS}_2$ , is easily soluble in alkalis, being more acidic than stannous sulphide.

#### COMPARATIVE STUDY OF TITANIUM, ZIRCONIUM, CERIUM, AND THORIUM

It has already been shown that titanium is more metallic than germanium; and, by inference, that zirconium, cerium, and thorium are, on the whole, more metallic and electropositive than tin and lead. It will therefore be of interest to inquire what sort of compounds are formed by these somewhat more electropositive metals, and how they compare with the compounds of germanium, tin, and lead.

With the possible exception of titanium these elements form no

gaseous hydrides; neither do they form organo-metallic compounds. Zirconium, however, forms a solid hydride,  $ZrH_2$ , and cerium a solid hydride, probably  $CeH_3$ .<sup>1</sup>

**Halides and the Question of Valency.** The following table includes representative halides:

Ti		Zr		Ce		Th	
$TiCl_3$	$TiCl_4$	$ZrCl_3$	$ZrCl_4$	$CeCl_3$	$CeCl_4$	$ThCl_3$	$ThCl_4$
$TiF_3$	$TiF_4$	$ZrF_3$	$ZrF_4$	$CeF_3$	$CeF_4$	$ThF_3$	$ThF_4$
$K_2TiF_6$	$(NH_4)_2TiCl_6$	$K_2ZrF_6$	$K_2ZrF_6$	$K_2CeF_6$	$K_2CeF_6$	$K_2ThF_6$	$K_2ThF_6$
		$Ni_2ZrF_6$					

At first sight the interpretation of the relationships here displayed appears difficult. Zirconium and thorium seem to be rigidly quadrivalent elements, but titanium appears also to be both bi- and trivalent, whilst cerium is trivalent in its stable halides, the tetrachloride  $CeCl_4$  being very unstable and prone to decompose into the trichloride and chlorine, though it forms complex salts of the type  $M_2CeCl_6$ .<sup>2</sup>

These two anomalies, viz. the lower valencies of titanium and the feeble quadrivalency of cerium, may be explained by considering the relationships of these elements to other elements in adjacent groups.

Following titanium in series are vanadium, chromium, and manganese; and no other elements are so rich in variety of compounds as these, on account of variable valency and transition from basic to acidic properties with increase of valency. It will now be seen that titanium is the first of a series of four elements— or five, if iron is included— with variable valency, which may be thus expressed:

Ti <sup>II</sup>	Ti <sup>III</sup>	Ti <sup>IV</sup>			
V <sup>II</sup>	V <sup>III</sup>	V <sup>IV</sup>	V <sup>V</sup>		
Cr <sup>II</sup>	Cr <sup>III</sup>		—	Cr <sup>VI</sup>	
Mn <sup>II</sup>	Mn <sup>III</sup>	Mn <sup>IV</sup>	—	Mn <sup>VI</sup>	Mn <sup>VII</sup>
Fe <sup>II</sup>	Fe <sup>III</sup>		—	Fe <sup>VI</sup>	

So is illustrated the relationship which elements may bear to their neighbours in series as well as in group— a fact which becomes more prominent in the region of the eighth group.

The feeble quadrivalency of cerium would seem to justify the exclusion of this element from Group IV altogether, and this anomaly must now be considered.

Both by natural occurrence and the properties of many of its compounds cerium is shown to be one of the rare earth metals. The line of these metals begins with scandium, descends the third group through yttrium and lanthanum, then passes to cerium in the fourth group, and thence through praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, erbium, thulium, ytterbium, and lutetium, to tantalum in the fifth group.

<sup>1</sup> Muthmann and Kraft, *Annalen*, 1902, 325, 265.

<sup>2</sup> J. Koppel, *Zeitsch. anorg. Chem.*, 1898, 18, 305.

The existence of these numerous, and generally very rare, metals between lanthanum in the third group and tantalum in the fifth is itself an anomaly so far as the periodic law is concerned; but in face of this anomaly it is not surprising that cerium is not a proper fourth-group element. No doubt its affinities lie with the third group, as is shown by the stability of its trivalent compounds. Consequently the detailed description of this element and its compounds will find a place in the volume dealing with the third group.

It is noteworthy that each of these four elements forms alkali salts of the complex acids  $H_2XF_6$ , and that silicon, germanium, and tin form similar compounds. Thus, with the exception of carbon and possibly of lead, every element of the fourth group forms these complex fluorides, which may therefore be regarded as fundamentally typical of the group.

Zirconium and thorium resemble each other in forming complex fluorides of other than the group type, but in every known halide and indeed in every known compound except  $ZrH_2$  and  $Zr_2O_3$ , these two metals are quadrivalent. This is a remarkable fact for which the periodic law can provide no parallel, and therefore no explanation. For it will be found on examination that there is no other element possessing a valency of four or more which does not exercise less than its typical valency in some of its compounds. In the case of zirconium this constant valency appears all the more remarkable when compared with that of titanium, which resembles the succeeding element vanadium in variable valency; for columbium, which follows zirconium, also shows variable valency.

A comparison of the tetrachlorides  $TiCl_4$ ,  $ZrCl_4$ ,  $(CeCl_4)_2$ , and  $ThCl_4$  will serve to illustrate the gradation of metallic properties.

Titanium tetrachloride,  $TiCl_4$ , is a liquid boiling at  $136^\circ C$ , which reacts with water with evolution of heat yielding first  $Ti_2O_3Cl_2$  and then  $H_2TiO_3$  by complete hydrolysis. Zirconium tetrachloride,  $ZrCl_4$ , is formed as a crystalline sublimate; it gives with water no crystalline hydrate but a soluble oxychloride,  $ZrOCl_2$ , and, by dialysis, the colloidal hydroxide,  $Zr(OH)_3$ .

Cerium tetrachloride,  $CeCl_4$ , is unstable; but thorium tetrachloride,  $ThCl_4$ , melts at  $820^\circ C$ , and easily dissolves in water, but with evolution of heat, thus showing a vestige of chloranhydride character; it forms the crystalline hydrates  $ThCl_4 \cdot 8H_2O$  and  $ThCl_4 \cdot 9H_2O$ , and the oxychlorides  $ThCl_4O \cdot 7H_2O$  and  $ThCl_4(OH)_2 \cdot 5H_2O$ , soluble in water.

Titanium tetrachloride,  $TiCl_4$ , dissolves in concentrated hydrochloric acid, forming  $H_2TiCl_6$ , which gives rise to a well-defined series of salts. Zirconium tetrachloride,  $ZrCl_4$ , has a much feeble power of forming complex salts;  $Na_2ZrCl_6$  is probably formed by heating its constituent salts together, and pyridine and quinoline salts of the same type exist.

Cerium tetrachloride,  $CeCl_4$ , forms complex salts  $M_2CeCl_6$ ; but thorium tetrachloride,  $ThCl_4$ , forms no inorganic salts of this type, though corresponding pyridine and quinoline salts are known.

All these facts illustrate a gradation from chloranhydride characters in titanium tetrachloride to almost completely saline characters in thorium tetrachloride.

It will be remembered that titanium is more electropositive than germanium, the corresponding element in the B subgroup. This relationship may be expected to extend throughout both subgroups to

thorium and lead respectively. Now, although lead tetrachloride is unstable, it is a liquid and readily combines with ammonium chloride to form ammonium plumbichloride,  $(\text{NH}_4)_2\text{PbCl}_6$ . Its same character is shown by these two facts to be inferior to that of thorium tetrachloride.

The relationships of the oxy-compounds of Group IV A may now be considered. They will be the easier to understand in view of the above study of the halides.

✕ OXY-COMPOUNDS OF GROUP IV A

Ti	Zr	Ce	Th
$\text{TiO}$ , $\text{Ti}_2\text{O}_3$ , $\text{TiSO}_4$ (?) $\text{Ti}_2\text{O}_3$ , $\text{Ti}(\text{OH})_3$ $\text{Ti}_2(\text{SO}_4)_3$ and double salts, $c, g$ $\text{M.Ti}(\text{SO}_4)_4$ $2\text{H}_2\text{O}$	$\text{Zr}_2\text{O}_3$	$\text{Ce}_2\text{O}_3$ , $\text{Ce}(\text{OH})_3$ $\text{Ce}_2(\text{SO}_4)_3$ various hydrates and double salts, but no alumn $\text{Ce}(\text{NO}_3)_3$ $\text{Ce}_2(\text{CO}_3)_3$	—
$\text{TiO}_2$ $\text{Ti}(\text{OH})_4$ , $\text{H}_2\text{O}$ $\text{Ti}(\text{SO}_4)_2$ , $\text{TiOSO}_4$	$\text{ZrO}_2$ , $\text{ZrO}_2 \cdot \text{H}_2\text{O}$ $\text{Zr}(\text{SO}_4)_2$ , $\text{ZrOSO}_4$	$\text{CeO}_2$ , $\text{Ce}(\text{OH})_4$ $\text{Ce}(\text{SO}_4)_2$	$\text{ThO}_2$ , $\text{Th}(\text{OH})_4$
$\text{K}_2\text{Ti}(\text{SO}_4)_2$	$\text{K}_2\text{Zr}(\text{SO}_4)_2$ $\text{K}_2\text{Zr}_2\text{O}_7(\text{SO}_4)_2$	$\text{K}_2\text{Ce}(\text{SO}_4)_2$ $2\text{Ce}(\text{SO}_4)_3$ , $\text{Ce}_2(\text{SO}_4)_3$ $\text{H}_2\text{SO}_4$ , $2\text{H}_2\text{O}$	$\text{Th}(\text{SO}_4)_2$ (various hydrates) $\text{K}_2\text{Th}(\text{SO}_4)_2$ $\text{K}_2\text{Th}(\text{SO}_4)_6$ $\text{Rb}_2\text{Th}(\text{SO}_4)_2$
$\text{Na}_2\text{TiO}_3$ , $\text{Mg}_2\text{TiO}_3$ , phosphates, $c, g$ $\text{K}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{P}_2\text{O}_5$	$\text{Zr}(\text{NO}_3)_4$ $\text{ZrO}(\text{NO}_3)_2$ $\text{Na}_2\text{ZrO}_3$ , $\text{CaZrO}_3$	$\text{Ce}(\text{NO}_3)_3$ $\text{K}_2\text{Ce}(\text{NO}_3)_6$ Neither $\text{Ce}_2\text{O}_3$ nor $\text{CeO}_2$ is acidic	$\text{Th}(\text{NO}_3)_4$ $\text{K}_2\text{Th}(\text{NO}_3)_6$ , etc. Basic carbonates $\text{K}_2\text{Th}(\text{CO}_3)_2$ $(\text{NH}_4)_2\text{Th}(\text{CO}_3)_2$ $\text{ThO}_2$ has no acidic properties
SUPEROXIDES AND ACIDS			
$\text{TiO}$ , $3\text{H}_2\text{O}$ or $\text{Ti}(\text{OH})_3$ , $\text{H}_2\text{O}$ , $c, g$ $\text{Na}_2\text{O} \cdot 2\text{Ti}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	$(\text{Zr}_2\text{O}_3)_2$ , $\text{ZrO}_3$ $\text{Zr}(\text{O}_2\text{H})(\text{OH})_2$ $\text{Na}_2\text{Zr}_2\text{O}_7$	$\text{CeO}_2$ , $\text{H}_2\text{O}$	$\text{Th}_2\text{O}_3$ , $\text{ThO}_3$ $\text{Th}(\text{OH})_3$ $\text{Th}(\text{O}_2\text{H})(\text{OH})_2$ $\text{Th}(\text{O}_2\text{H})(\text{OH})_3$ No salts

**The Lower Oxides and their Salts.** Titanium monoxide resembles germanium monoxide in scarcely forming oxy-salts, for both oxides are but feebly basic. Attention has already been drawn to the non-existence of lower compounds of zirconium and thorium. It is remarkable that this subgroup furnishes no analogues to the monoxides of tin and lead and their salts.

**The Sesquioxides.**—The sesquioxides  $\text{Ti}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  differ in the properties of the salts they form.  $\text{Ti}_2(\text{SO}_4)_3$  differs from the sulphates of Group III A, but resembles  $\text{V}_2(\text{SO}_4)_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{Mn}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{Cr}_2(\text{SO}_4)_3$  in forming an alumn. Thus the relationship between this series of consecutive polyvalent elements is further exemplified. No nitrate or carbonate of  $\text{Ti}^{\text{III}}$  is known, and the sulphide  $\text{Ti}_2\text{S}_3$  is formed only in the dry way. Nevertheless  $\text{Ti}_2\text{O}_3$  displays no acidic power.

$\text{Ce}_2\text{O}_3$  and its salts resemble the corresponding compounds of Group III A, and are indeed typical rare earth compounds. Thus the oxides  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$  all form double sulphates which are not alums.

**The Dioxides.**—The oxides  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , and  $\text{ThO}_2$  show an increase of basic power from Ti to Th, and a corresponding diminution of acidic power. Thus  $\text{Ti}^{IV}$  and  $\text{Zr}^{IV}$  form definite basic sulphates, such as are not formed by  $\text{Ce}^{IV}$  and  $\text{Th}^{IV}$ ; though  $\text{Th}(\text{SO}_4)_2$  has an acid reaction in solution and hydrolyses cane-sugar and methyl acetate. The power to form double sulphates, which persists to  $\text{Th}^{IV}$ , shows the presence of feebly acidic properties.  $\text{Th}^{III}$  is not known to form a nitrate or carbonate, probably not being basic enough. Nitrate appears with  $\text{Zr}^{IV}$  and also a basic nitrate,  $\text{ZrO}(\text{NO}_3)_2$ , as might be expected; whilst a characteristic of  $\text{Ce}^{IV}$  and  $\text{Th}^{IV}$  is the formation of the double or complex nitrates  $\text{K}_2\text{Ce}(\text{NO}_3)_6$  and  $\text{K}_2\text{Th}(\text{NO}_3)_6$ .  $\text{Th}^{IV}$  alone forms a carbonate, which is basic, and several double carbonates.

The acidic properties of the dioxides are very instructive. Although titanium dioxide is much more basic than silica, the titanic acids resemble the silicic acids. Orthotitanic acid can exist in colloidal suspension, metatitanic acid is a gelatinous precipitate. Each variety of acid forms salts, and phosphosilicates correspond to the phosphotitanates. The acidic properties of  $\text{ZrO}_2$  are of the feeblest description. By fusion of this oxide with basic oxides salts of somewhat indefinite composition are obtained, which are hydrolysed by water. A similarity between zirconates and silicates is, however, shown by the existence of silico-zirconates,  $\text{K}_2(\text{SiO}_3\text{ZrO}_3)$ .  $\text{ZrO}_2$  is a feebler acidic oxide than  $\text{TiO}_2$ , and with  $\text{ZrO}_2$  acidic properties end; neither  $\text{CeO}_2$  nor  $\text{ThO}_2$  is acidic.

**The Superoxides.** The formation of superoxides, *i.e.* derivatives of hydrogen peroxide, in which the valency of the metal is not increased, is a characteristic which sharply differentiates the metals of Subgroup IV B from those of Subgroup IV A. That the power to form a superoxide is connected with the electropositivity of the metal is shown by the fact that the most stable superoxides are formed by the most electropositive metals, *i.e.* the metals of the alkalis and alkaline earths.

Lanthanum forms the superoxide  $\text{La}_2\text{O}_5$ , and thus the metals of Group IV A are connected through the third group with the alkaline earth metals as regards this property.

## CHAPTER II

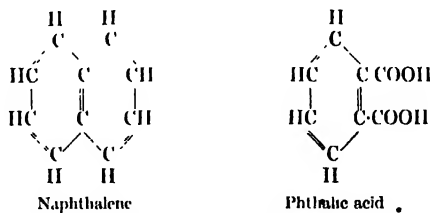
### CARBON AND ITS COMPOUNDS

#### CARBON

Symbol, C. Atomic weight, 12.005 (O = 16)

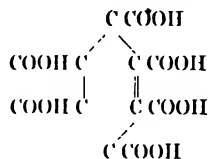
**General.** The element carbon is widely distributed throughout the visible universe. Its presence in the cooler stars has been revealed by spectrum analysis, and its cosmic distribution is indicated by its occurrence in meteorites. Most, if not all, of the carbon in the free and combined state in the world was originally present as atmospheric carbon dioxide. Thence, through the medium of water, it passed into combination with basic oxides to form mineral carbonates, which constitute a considerable part of the crust of the earth. With the appearance of vegetable life the diminution of atmospheric carbon dioxide continued, "organic" compounds were formed, and carbon was liberated in the free state. Henceforth the element performed a twofold function—as the material basis of living organisms and as a carrier of energy. The former function was possible to carbon alone because of the particular degree of reducibility of carbon dioxide and of the unique power possessed by this element of combining with itself, and with hydrogen, oxygen, nitrogen, sulphur, and other elements, to form the innumerable compounds of "organic" chemistry. The latter function depends upon the fact that the reduction of atmospheric carbon dioxide by plants is accompanied by the absorption of solar energy, which is thus stored up in wood, coal, and other combustible material, and is then available in the form of solid, liquid, or gaseous fuel to meet the manifold needs of human civilisation.

**Molecular State of Carbon.** The vapourisation temperature of carbon is exceedingly high, and consequently the vapour density of this element has never been ascertained. Carbon, however, dissolves in molten iron, and it would appear that this fact might furnish a cryoscopic method of ascertaining its molecular weight. But a carbide of iron, and not free carbon, exists in such solution.<sup>1</sup> A hint of the molecular state of carbon is given by the production of mellitic or benzene-hexacarboxylic acid,  $C_6(COOH)_6$ , from charcoal by oxidising agents. Since phthalic acid is derived from naphthalene by oxidation thus:

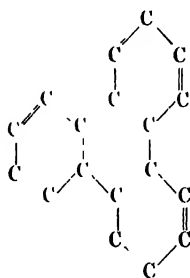


<sup>1</sup> Roozeboom, *Zeitsch. physikal. Chem.*, 1900, 34, 436

it may be presumed that benzene-hexacarboxylic acid—

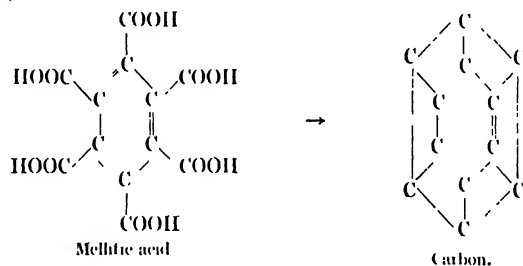


is derived from a benzene nucleus surrounded by three other benzene rings thus <sup>1</sup>:

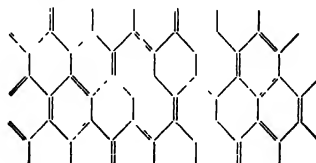


It is possible, therefore, that solid carbon is built up of benzene nuclei after this fashion.

Dewar <sup>2</sup> derives the constitution of the carbon molecule from mellitic acid, thus:



but Aschan <sup>3</sup> considers that this view does not harmonise with Baeyer's strain theory, and proposes the following constitution for the molecule of carbon in wood charcoal:



<sup>1</sup> Schultz, *Ber.*, 1871, 4, 802-803.

<sup>2</sup> Dewar, *Chem. News*, 1908, 97, 16.

<sup>3</sup> Aschan, *Chem. Zeit.*, 1909, 33, 561.

Dunroth and Kerkovius,<sup>1</sup> however, bring evidence to show that a molecule of carbon contains  $C_6$ -rings as well as benzene rings. Hans Meyer,<sup>2</sup> on the other hand, regards each of the forms of carbon as an aggregation of particles of various sizes, and consequently discounts the value of theories as to the structure of the carbon molecule.

**Valency of Carbon.** The study of the compounds of carbon played a very important part in the development of the doctrine of valency. Consequent upon his researches on fulminate of mercury, Kekulé<sup>3</sup> added to the types of Gerhardi another type, that of marsh gas, which at first he wrote  $C_2H_4$  ( $C = 6$ ), but afterwards recognised that in this compound 1 atom of carbon ( $C = 12$ ) combines with four atoms of hydrogen. Thus, in extending the doctrine of valency which had been brought forward by Frankland, he declared the carbon atom to be quadrivalent. "If we look at the simplest compounds of this element,  $CH_4$ ,  $CH_3Cl$ ,  $CCl_4$ ,  $CHCl_3$ ,  $COCl_2$ ,  $CO_2$ ,  $CS_2$ , and  $CHN$ , we are struck by the fact that the quantity of carbon which is considered by chemists as the smallest amount capable of existence—the atom—always binds four atoms of a monatomic or two of a diatomic element, so that the sum of the chemical units of the elements combined with one atom of carbon is always equal to four. We are thus led to the opinion that carbon is tetratomic."<sup>4</sup> Kolbe<sup>5</sup> and Frankland arrived at similar ideas, as well as Couper,<sup>6</sup> to whom we owe the expression of graphic formulae by bonds.

Kekulé was an advocate of constant valency.<sup>7</sup> According to him the "atomicity of the elements is a fundamental property of the atoms, quite as unalterable as their atomic weights." Therefore Kekulé could not admit the valency of carbon ever to be less than four.

On the other hand, the valency of many elements is known to be variable, and to rise to a maximum corresponding to the group of the periodic system to which the element in question belongs. Whether or not carbon is ever less than quadrivalent may therefore be discussed.

In carbon monoxide the carbon atom is usually considered to be bivalent, thus:  $C \equiv O$ , and Kekulé and Kolbe reconciled this belief with the theory of constant valency, by assuming that the two remaining carbon valencies satisfied each other. Since it was discovered, however, that oxygen may be quadrivalent,<sup>8</sup> it has been assumed that the four carbon valencies are satisfied thus:  $C \equiv O$ , though it does not appear how these four valencies, which are supposed to be directed through the angular points of a tetrahedron, can be so far "strained" as to meet in a single atom of oxygen.

Friend<sup>9</sup> modifies this view by his theory of latent valencies, and assumes that the four carbon valencies are satisfied with two free and two latent oxygen valencies.

<sup>1</sup> Dunroth and Kerkovius, *Annalen*, 1913, 399, 120

<sup>2</sup> Hans Meyer, *Monatsh.*, 1914, 35, 163

<sup>3</sup> Kekulé, *Annalen*, 1857, 101, 200, 104, 129

<sup>4</sup> Kekulé, *Ueber die Konstitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs*, 1858

<sup>5</sup> Kolbe, *Annalen*, 1857, 101, 262

<sup>6</sup> Couper, *Compt. rend.*, 1858, 46, 1157

<sup>7</sup> Kekulé, *Zeitsch. Chem.*, 1861, p. 689

<sup>8</sup> Collie and Tickle, *Trans. Chem. Soc.*, 1899, 75, 710

<sup>9</sup> Friend, *Trans. Chem. Soc.*, 1908, 93, 269, *The Theory of Valency* (Longmans & Co.), 1909.



The validity of these theories is contingent upon our knowledge of the nature of valency itself. Meanwhile it is pertinent to ask whether any real chemical difference is indicated between the formulae  $C \equiv O$  and  $C = O$ .

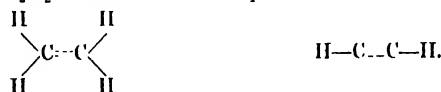
Fulminic acid may be regarded as the oxime of carbon monoxide, and so may contain bivalent carbon, thus:  $C \equiv NOH$ .<sup>1</sup> Similar isonitriles and isocyanides,  $C \equiv NR$ , may contain bivalent carbon; also hydrocyanic acid itself if, as is possible, it has the constitution  $HN \equiv C$ .

If, however, nitrogen is assumed to be quinquivalent, carbon may still be quadrivalent in these compounds.

In the year 1900 Gomberg<sup>2</sup> discovered "triphenylmethyl," to which he attributed the formula  $C(C_6H_5)_3$ , suggesting that carbon is tervalent in this compound. Tschitschibabin<sup>3</sup> regards the compound as hexaphenylethane  $(C_6H_5)_3C \cdot C(C_6H_5)_3$ , and this view is supported by the researches of Piccard<sup>4</sup> and of Schlenk and his co-workers,<sup>5</sup> from which it appears fairly certain that in the solid condition the compound corresponds to the double formula, whilst in solution in organic liquids it dissociates into triphenylmethyl.

A number of carbon compounds exist, in each of which an atom of carbon is attached to fewer than four other atoms or groups - one of which, however, is another carbon atom. These compounds are all unsaturated; that is to say, they easily combine with other atoms or groups to produce compounds in which each of their carbon atoms has four separate points of attachment. It is not usual to regard the valency of carbon in these compounds as less than four, double or triple bonds being employed to satisfy the valencies.

The simplest examples of such compounds are ethylene,  $C_2H_4$ , and acetylene,  $C_2H_2$ , which are usually represented thus:



Now it is not justifiable to introduce double and triple bonds in order to satisfy a preconceived opinion that carbon must needs be quadrivalent. Hinrichsen,<sup>6</sup> indeed, objects to the use of double bonds; and if valency is regarded simply as the measure of the number of other atoms or groups with which an atom is combined in a particular compound his objection is valid, and carbon becomes trivalent in ethylene and bivalent in acetylene; and it might even be urged that both carbon and oxygen are univalent in carbon monoxide.

To discredit this view, therefore, it is necessary to show that double and triple bonds have more than a pictorial significance, and this can easily be done.

Thus the potential valencies of the two carbon atoms which remain inoperative in ethylene, for example, are not independent of each other; one cannot be saturated without the other, so that no such compound as  $CH_2-CH_2Cl$  exists. It may be that the saturation of both carbon

<sup>1</sup> Nef, *Annalen*, 1891, 280, 303.

<sup>2</sup> Gomberg, *Ber.*, 1900, 33, 3150.

<sup>3</sup> Tschitschibabin, *Ber.*, 1901, 37, 4709; 1905, 38, 771.

<sup>4</sup> Piccard, *Annalen*, 1911, 381, 31.

<sup>5</sup> Schlenk, Weckel, and Herzenstein, *Annalen*, 1910, 372, 1.

<sup>6</sup> Hinrichsen, *Zeitsch. physikal. Chem.*, 1902, 39, 305; *Annalen*, 1904, 336, 175; *Ueber den gegenwärtigen Stand der Valenzlehre* (Stuttgart, 1902).

atoms simultaneously is necessary for molecular stability, but if so, the fact is better expressed by the double bond than by representing each carbon atom as separately tervalent. Moreover, when the elements of a halogen hydride are removed from an alkyl halide to produce an unsaturated hydrocarbon, it is always two adjacent carbon atoms which yield these elements. This would not appear necessary on the assumption that *any* carbon atom in a carbon chain might become tervalent, but is necessary if loss of halogen hydride involves double linkage between two adjacent atoms. Propylene, for example, is formed by the elimination of HI from either normal or iso-propyl iodide,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$  or  $\text{CH}_3\text{CHI}\text{CH}_3$ ; consequently propylene must contain a methyl ( $\text{CH}_3$ ) group, and cannot be  $\text{CH}_2\text{CH}_2\text{CH}_2$ , but is necessarily  $\text{CH}_3\text{CH}=\text{CH}_2$ . Thus it is two adjacent carbon atoms that remain unsaturated in propylene, and this fact may therefore be expressed by the double bond, and the formula for propylene be written  $\text{CH}_3\text{CH}=\text{CH}_2$ .

That the mode of linkage between two adjacent carbon atoms which are unsaturated is really different from that between carbon atoms which are saturated is shown by the fact that when oxidation which involves rupture takes place, this rupture always occurs at the double bond. The relative weakness of the double bond is accounted for by Baeyer's tension or strain theory, to which reference will shortly be made.

If carbon is admitted to be quadrivalent in unsaturated compounds such as the above, then, with the few exceptions already considered, carbon is always quadrivalent; for it does not appear that the valency of this element ever exceeds four.

Nevertheless Thiele<sup>1</sup> has introduced a theory of *partial valencies* to account for the reactivity of atoms joined by double bonds, and especially of such carbon atoms in chain and ring compounds.

An example of the reduction of a chain compound will illustrate Thiele's theory.

Mucic acid:

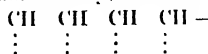


yields on partial reduction:

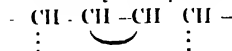


and the problem is to account for the remaining double bond taking the central position in the chain.

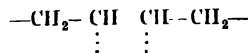
According to Thiele the carbon atoms possess partial valencies over and above their quadrivalency, which are represented thus:



The partial valencies of adjacent carbon atoms are, however, conjugated, and the above system may be represented thus:

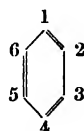


So the way is prepared for the appearance on reduction of a double bond between the central carbon atoms, thus:



<sup>1</sup> Thiele, *Annalen*, 1899, 306, 87.

Thiele has also applied his theory to the constitution of benzene, which according to Kekulé's formula —



shows a difference between the 2 and 6 positions on account of the arrangement of the double bonds, unless these are supposed to oscillate. Thiele introduces partial valencies to conjugate the carbon atoms united by single bonds, and thence derives a symmetrical formula, thus :

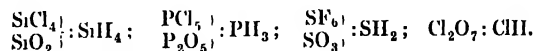


This, however, appears to amount to making carbon quinquivalent. Tschitschibabin<sup>1</sup> has discussed the various explanations which have been given of the unsaturated character of the carbon atom in different classes of organic compounds; and concludes that the numerical value of the valency of an atom is simply expressed by the number of other atoms with which it combines. Thus, for example, carbon becomes tervalent in ethylene and bivalent in acetylene.

The question of the equality of the four carbon valencies may be briefly mentioned. It has been investigated by Popoff<sup>2</sup> and Geuther,<sup>3</sup> and by Henry,<sup>4</sup> who proved the equality of the four carbon valencies in nitromethane by preparing this substance by four distinct processes, so arranged that a different hydrogen atom should be replaced in each process.

The qualitative aspect of valency may here be considered, so far as it applies to carbon.

It is well known that many elements display reciprocal powers of combination with oxygen or halogen on the one hand and hydrogen on the other, the sum of the valencies in the two classes of compound being equal to 8. Thus there are the following compounds :



Having regard to these relationships, Abegg<sup>5</sup> introduced the theory that every element possesses a maximum valency of 8, made up of

<sup>1</sup> Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1690.

<sup>2</sup> Popoff, *Annalen*, 1868, 145, 283.

<sup>3</sup> Geuther, *Annalen*, 1880, 205, 223, 227; 1883, 218, 12; 1887, 240, 192, 225.

<sup>4</sup> Henry, *Compt. rend.*, 1887, 104, 1106; *Zeitsch. physikal. Chem.*, 1888, 2, 553.

<sup>5</sup> Abegg, *Zeitsch. anorg. Chem.*, 1904, 39, 330.

positive and negative or normal and contra valencies, as in the following series :

	Na	Mg	Al	Si	P	S	Cl
Normal valencies	+ 1	+ 2	+ 3	+ 4	+ 3	+ 2	+ 1
Contra valencies	- 7	- 6	- 5	- 4	- 3	- 2	- 1

In the first three elements of this series the contra valencies are latent, in the last three they correspond to the powers of combination of the elements with hydrogen. Silicon, occupying a central position in the series, has normal and contra valencies numerically equal, as shown, for example, in  $\text{SiCl}_4$  and  $\text{SiH}_4$ . Nevertheless, judging by the relative stabilities of the compounds, the + valencies of silicon, as manifested towards chlorine, are stronger than the - valencies, as manifested towards hydrogen. Now as regards carbon the + and - valencies appear to be, not only numerically equal, but also equal in strength. It was this fact which lay at the basis of Dumas' demonstration of substitution,<sup>1</sup> by which it was shown that chlorine could displace hydrogen from a carbon compound without disturbing the stability of the compound or fundamentally altering its nature. And not only can carbon form stable compounds in which its atoms are linked with hydrogen or chlorine or both, but also stable compounds containing oxygen, nitrogen, sulphur, and other elements, including metals joined to carbon.

More fundamental, perhaps, than the power possessed by carbon of forming stable compounds with such a variety of elements is that qualitative property of the carbon valencies which enables the atoms of this element to combine with one another in chains and rings. This property, which may perhaps be regarded as a manifestation of neutral rather than + or - valency, has been shown by Martin<sup>2</sup> to be deducible from a study of the affinities of the elements of the series which contains carbon.

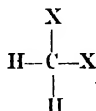
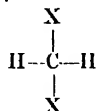
By collecting the thermal and other data regarding the combination of each of the elements with as many other elements as possible, and erecting perpendiculars representing affinities, as shown by heats of formation, stabilities, etc., from the loci of these other elements on the periodic diagram, Martin has produced an "affinity surface" for each element, a glance at which shows the elements with which a particular element most readily combines. Thus in the series Li F the affinity surface of lithium rises to a maximum altitude over fluorine and the other halogens, but on traversing the series to the right the affinity peak is seen to travel to the left, till in the case of fluorine it rests over the alkali metals. The affinity surface for carbon shows a steep peak over carbon itself, and a lesser altitude over oxygen. Thus it appears from the affinity surface for carbon, and consequently from the experimental facts on which it is constructed, that this element manifests a greater affinity for itself than for any other element. In this respect carbon is quite alone; and thus is furnished a striking commentary upon the combining capacity of carbon atoms for each other, on which property more than any other the facts of organic chemistry are based.

There remains to be considered one other aspect of the valency of

<sup>1</sup> Dumas, *Ann. Chim. Phys.*, 1834, [n], 56, 113, 140.

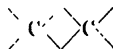
<sup>2</sup> Martin, *Researches on the Affinities of the Elements* (Churchill), 1905, p. 187. See this series, vol. viii, pp. 16 et seq.

the carbon atom, *i.e.* the direction in space in which the units of valency are exercised. That they do not all lie in one plane—being directed, for example, towards the corners of a square—is made evident by the non-existence of two di-derivatives of methane, which might be formulated thus:

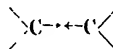


Kekulé, in 1867,<sup>1</sup> suggested that the four valencies end in the faces of a tetrahedron; Paterno,<sup>2</sup> in 1869, explained the isomerism of the compounds  $\text{C}_2\text{H}_2\text{Br}_2$  by assuming that the carbon valencies are directed towards the corners of a tetrahedron, and in the same year J. Wislicenus<sup>3</sup> spoke of "Chemistry in Space"; whilst in 1871 Le Bel<sup>4</sup> and van't Hoff,<sup>5</sup> the former a disciple of Pasteur, the latter of Kekulé, established the stereochemical<sup>6</sup> theory of the carbon atom by employing it to explain optical isomerism.

According to van't Hoff's presentation of the theory, the carbon atom appears to be a point at the centre of a regular tetrahedron, towards the angular points of which the valencies act as four equal forces. It has been shown, however, by Auwers<sup>7</sup> that this view is mechanically inadequate, for two of the forces acting from each carbon atom thus:



would be resolved along a straight line joining the carbon atoms when union took place, thus:



This, however, is not the case, for the double bond between two carbon atoms cannot be represented as acting along a single line.

Le Bel<sup>8</sup> has conceived that each of four atoms approaching a carbon atom is bounded in its influence by a sphere, and that these spheres meet each other around the carbon atom just as four equal spheres may lie against each other, so that lines joining their centres form a regular tetrahedron. Thus the valencies act as before towards the angular points of a tetrahedron; but the carbon atom at its centre is not necessarily a point.

The Strain or Tension Theory of Baeyer,<sup>9</sup> which has been of much value in the study of cyclic carbon compounds, is expressed as follows:

"The four valencies of a carbon atom act parallel to lines joining

<sup>1</sup> Kekulé, *Zeitsch. Ch.*, 1867, N F 3, 217.

<sup>2</sup> Paterno, *Giorn. ds Sci.*, 1869, *Naturali ed Econ.*, vol. v, Palermo, *Gazzetta*, 1893, 35.

<sup>3</sup> Wislicenus, *Ber.*, 1869, 22, 620.

<sup>4</sup> Le Bel, *Bull. Soc. chim.*, 1874, [2], 22, 377.

<sup>5</sup> *La Chimie dans l'Espace*, 1874, [2], 22, 377. see also J. H. van't Hoff, *The Arrangement of Atoms in Space* (Longmans, 1898).

<sup>6</sup> stereoisomerism.

<sup>7</sup> Auwers, *Die Entwicklung des Stereoisomerismus*.

<sup>8</sup> Le Bel, *Bull. Soc. chim.*, 1890, [3], 30, 1890, p. 22.

<sup>9</sup> Baeyer, *Ber.*, 1885, 18, 277.

the corners of a tetrahedron with its centre, making an angle of  $109^{\circ} 28'$  with one another. The direction of the valencies can be altered, but any such alteration produces a strain whose amount is proportional to the angle through which the valencies are diverted."

The above brief account of the stereochemistry of carbon suffices to show the lines on which the theory has developed. For the application of the theory to the constitution and properties of carbon compounds, books on organic chemistry must be consulted.

#### ALLOTROPIC FORMS OF CARBON

Carbon exists in two distinct crystalline forms, Diamond and Graphite, as well as in the amorphous state.

##### DIAMOND

**History.** Diamonds have been known and valued from antiquity for their brilliance and hardness. They were first called *Adamant*, whence *diamant*, *diamant*, *diamond* in A.D. 16. Pliny, A.D. 100, refers to the diamond as "the most valuable of gems, known only to kings." The gem was probably unknown to the early Hebrews, although the word is applied in Exodus xxxix, 11, to an engraved stone.

Diamonds were first discovered in the sands of India, whence they were brought to Europe in the time of the Romans. Their beauty and rarity gave rise to the superstitious belief that they could avert insanity, ward off the effect of poison, and restore domestic peace. Diamond was at one time thought to be a fossil resin or an "unctuous substance coagulated." On this account Newton believed diamond to be combustible; and the fact was first proved by the Florentine Academicians in 1694. It was observed in 1751 that diamonds disappear when heated in a furnace, while rubies remain unchanged; but Darcel and Rouelle showed in 1766 that this is not the case if the precious stones are first placed in a hermetically sealed vessel. Macquer, Cadet, and Lavoisier, about 1771, proved that diamond undergoes true combustion, burning with a flame; and, in conjunction with Brisson and Baumé, they ignited diamond, confined with air over mercury, by means of a burning-glass, and showed the formation of carbon dioxide.

Thus the nature of diamond was established; whilst its chemical identity with charcoal was proved by Smithson Tennant, who in 1797 obtained equal weights of carbon dioxide from equal weights of charcoal and diamond. Lastly, Sir Humphry Davy showed in 1814 that the carbon dioxide produced by burning diamond is pure, containing no water; and therefore that diamond contains no hydrogen.

**Occurrence and Mining.** -Diamonds have been found in India, Brazil, South Africa; also in Borneo, Australia, Tasmania, North America, Guiana, and the Ural Mountains. India was the first diamond field, whence all the stones came in ancient times. The industry was centred in Golconda, which was a fortress and market for the gems, and gave its name to the adjacent mines. The discovery of diamonds in Brazil in 1725 struck a blow at the Indian industry. Tepico, afterwards named Diamantina, in the province of Minas Geraes, is the most important Brazilian centre. It is situated on a mountainous plateau consisting of laminated micaceous rock, flexible sandstone called *itacolumite*, and conglomerate. The diamonds are found on the plateau

and in the river gravels beneath it. Since 1844 diamonds have also been found in the neighbouring province of Bahia. In 1867 a pebble with which a child was playing on the banks of the Orange River was discovered to be a diamond, and two years afterwards a stone weighing  $83\frac{1}{2}$  carats, found in the same locality, was sold as the "Star of South Africa" for £25,000. "River diggings" commenced and the South African industry became established. Besides occurring in alluvial deposits, diamonds are found in South Africa in a kind of clay, called "yellow earth," fifty feet thick; and in a bluish-green rock of the nature of serpentine, known as "blue ground," which occurs beneath the "yellow earth" at Kimberley and Dutoitspan. This "blue ground" is in funnel-shaped deposits or "pipes" which are supposed to have been produced by volcanic outbursts during the cretaceous period. Formerly the earth was brought up from the open mines in buckets swung on ropes which formed a network overhead, but on account of the danger from landslips this method has been superseded by the sinking of shafts through the adjacent rock combined with tunnels. After concentration the earth is washed down a greased surface to which the diamonds adhere.

**Description.**—Diamonds vary greatly in size. The Cullman diamond, the largest ever found, which was discovered in 1905 in the yellow ground at the Premier mine, in the Transvaal, weighed  $3025\frac{1}{2}$  carats <sup>1</sup> ( $1\frac{1}{2}$  lb.). Rough, small diamonds, consisting of impure crystals or fragments, are known as *Bort* or *Baort*; black diamond is *Carbonado*. A specimen of carbonado found in Bahia in 1895 weighed 3078 carats. The most valuable diamonds, those of the "purest water," are colourless, transparent and brilliant. One of the most beautiful of these is the Pitt or Regent diamond, weighing 136.25 carats. The celebrated Koh-i-noor, a British crown diamond, which came from India, originally weighed 186 carats, but was reduced by cutting to 106 carats. Diamonds may be cloudy or tinted grey, yellow, or brown; they may also be coloured red, green, or blue by traces of metallic oxides. The Hope diamond, which weighs  $41\frac{1}{2}$  carats, is blue, and is worth £25,000.

It has been discovered by Sacerdote <sup>2</sup> that exposure to cathode rays deepens the original colour of the diamond. This deepening of colour appears to be permanent at ordinary temperature, but exposure to a temperature of  $300^{\circ}$ – $400^{\circ}$  C. converts the diamond to its original colour.

**Physical Properties of Diamond and Carbonado.**—*Crystalline Form.*—Diamonds are often found in perfect crystals which belong to the regular system, being modifications of the tetrahedron or octahedron, such as the rhombic dodecahedron, hexakis tetrahedron, and hexakis octahedron. South African diamonds are generally octahedral, Brazilian cubical. Sometimes interpenetration or twinning of crystals is observed. The faces of the crystals are often rounded; the fracture may be conchoidal. Cleavage also takes place along directions parallel to the crystal faces. It is the work of the lapidary to cut and polish the diamond so as to develop the brilliancy of the crystal faces. This is done by pressing the surface of the stone against a revolving metal wheel on which is diamond dust mixed with oil.

<sup>1</sup> Carat (*κεράτιον*) = the seed of St John's bread, formerly used for weights. 1 diamond carat = 3.17 grains or 0.2051 grm. 1 oz troy = 161.5 carats.

<sup>2</sup> Sacerdote, *Compt. rend.*, 1909, 149, 993.

**Hardness.**—The diamond is the hardest known substance; it is "adamant." Its hardness is reckoned 10 on the mineralogist's scale.<sup>1</sup> Nevertheless metallic tantalum and its alloy compete with diamond in hardness, and beryl and sapphire of carbon abrade the diamond. Different diamonds differ in hardness; e.g. those from Borneo are said to be harder than those from Australia, and Australian diamonds are harder than African. Different faces of the same diamond also differ in hardness. Carbonado is harder than colourless diamond.

**Density.**—The density of the diamond approximates at atmospheric temperature to 3.5, the highest observed value being 3.56 and the average about 3.52. Carbonado, which contains about 2 per cent. of impurity, has a density of 3 to 3.5.

**Optical Properties.**—The brilliant lustre and play of colours exhibited by the diamond are due to its high refractive<sup>2</sup> and dispersive power. The refractive index of diamond for sodium light is 2.417. The brilliance of the gem is due to total reflection of light within it on account of its high refractive power; for light incident at the surface from within at an angle greater than  $24\frac{1}{2}^\circ$  is reflected back into the stone. The corresponding angle for glass is  $40\frac{1}{2}^\circ$ . The dispersive power of the diamond is shown by comparing its refractive indices for red and blue light, which are 2.402 and 2.460 respectively. Diamonds are sometimes doubly refractive on account of internal strain. From the same cause they may explode spontaneously. Diamond shows absorption bands,<sup>3</sup> and those at the blue end of the spectrum are supposed to be due to some rare element such as samarium. Diamond is transparent to Röntgen rays, to which paste imitations are opaque.

Bovey, in 1663, observed that diamond phosphoresces in the dark by friction; it is luminous also after exposure to sunlight, and phosphoresces strongly under the influence of kathode, Röntgen, Becquerel and radium rays.

The radiation spectrum of diamond glowing in a Crookes' tube is continuous, with intensive lines in the green at  $537\text{ m}\mu$ , and in the blue at  $513\text{ m}\mu$  and  $503\text{ m}\mu$ .<sup>4</sup> During this treatment the stone becomes superficially coloured and changed into graphite,<sup>5</sup> and the same effect is produced by the prolonged action of radium. A pale yellow diamond was changed to bluish-green when embedded in radium bromide for eleven weeks.

The coefficient of linear expansion of the diamond is 0.00000118 at  $40^\circ\text{C}$ . and 0.00000132 at  $50^\circ\text{C}$ .<sup>6</sup> and becomes continuously less as the temperature falls. The compressibility between 100 and 500 atmospheres is  $5 \times 10^{-7}$  vol./atm.

The specific heat of diamond varies much with temperature. According to H. F. Weber<sup>7</sup> its value may be calculated from the interpolation formula

$$\gamma = 0.0947 + 0.000994t - 0.00000036t^2.$$

<sup>1</sup> Moh's scale, largely used by mineralogists, is as follows: (1) Talc, (2) Gypsum, (3) Calc. spar, (4) Fluor-spar, (5) Apatite, (6) Orthoclase, (7) Quartz, (8) Topaz, (9) Corundum, (10) Diamond.

<sup>2</sup> Vide F. F. Materns, *Deutsche Annalen*, 1902, 8, 464.

<sup>3</sup> K. Ångström, *Öfvers. K. Vet.-Akad. Förh.*, 1890, Nr. 7, 331.

<sup>4</sup> Crookes, *Proc. Roy. Soc.*, 1901, 74, 47.

<sup>5</sup> Cf. Swinton, *Proc. Roy. Soc.*, 1909, A, 82, 176.

<sup>6</sup> Euzéu, *Pogg. Annalen*, 1869, 138, 26.

<sup>7</sup> Weber, *Ber.*, 1872, 5, 303; *Pogg. Annalen*, 1875, 154, 367. See vol. I, p. 90.



whence the following values are obtained :

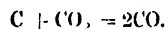
t° C.	0°	50°	100°	150°	200°
$\gamma$	0.0017	0.1135	0.1905	0.2357	0.2791

At low temperatures the specific heat is much diminished,<sup>1</sup> and at the temperature of liquid hydrogen it is only about one-twentieth of its value at atmospheric temperature.

**Conductivity for Heat and Electricity.**—Diamond is a good conductor of heat, and feels colder than glass ; it is, however, a bad conductor of electricity, thus differing from graphite.<sup>2</sup>

**Action of Heat upon, and Combustion of, the Diamond.**—Diamond is unchanged when heated to whiteness in hydrogen, but swells up and is converted into graphite when placed between the carbon poles of an electric arc. Diamond commences to form carbon dioxide when heated to 720° C. in oxygen ; the rate of combustion increases up to 800° C., when a flame appears and the mass becomes incandescent. A minute reddish ash remains, which amounts to from 0.05 to 0.2 per cent. of the original weight of the diamond, and consists of ferric oxide and silica, generally also with lime and magnesia.

**Action of Chemical Reagents on the Diamond.**—The diamond is scarcely attacked by any chemical reagent. It is stable towards chlorine, hydrochloric, hydrofluoric, and sulphuric acids at all temperatures, as well as towards a mixture of nitric acid and potassium chlorate, which dissolves graphite. Fusion with sodium or potassium carbonate, however, converts diamond into carbon monoxide by the reaction<sup>3</sup>



**Origin of the Diamond.**—The occurrence of the diamond in alluvial deposits and clays, accompanied by quartz, topaz, tourmaline, rutile, zircon, garnet, etc., throws no light upon the origin of this precious stone, since the crystals are loose and have evidently been borne away by natural agency from their place of origin. Small diamonds have, however, been found embedded in crystals of xanthophyllite, a siliceous mineral, in such a manner as to suggest that they originated there. Moreover, the diamonds in different "pipes" of blue ground in South Africa differ in quality ; and this suggests that they may have been formed in the pipes, perhaps by volcanic agency. Diamonds have also been found in meteoric stones, and in meteoric iron accompanied by carbonado and graphite. It therefore seems probable that diamonds have crystallised under suitable conditions from a solution of carbon in a siliceous or metallic solvent. The discovery of diamond, accompanied by carbonado and graphite, in a meteorite found in the Diablo Cañon,<sup>4</sup> and its study by Moissan, have thrown much light on the problem and enabled this chemist to prepare small diamonds artificially.

**Preparation of Artificial Diamond.**—The preparation of artificial diamonds from carbon is a problem which has long fascinated the minds of scientific men and others.

Despretz<sup>5</sup> in 1849 tried to make diamonds by means of an electric

<sup>1</sup> See also Dewar, *Proc. Roy. Soc.*, 1905, A, 76, 236.

<sup>2</sup> Cf. Koenigsberger, *Ber. Deut. physikal. Ges.*, 1912, 14, 8.

<sup>3</sup> Colomba, *Atti R. Istit. Lincei*, 1915, [v], 24, 1, 1137.

<sup>4</sup> Friedel, *Compt. rend.*, 1893, 116, 290 ; Moissan, *Compt. rend.*, 1893, 116, 288.

<sup>5</sup> Despretz, *Compt. rend.*, 1849, 28, 755, 29, 48, 545, 709.

are formed between a carbon rod and a bunch of platinum wire, and obtained a crystalline dust which scratched ruby. Hannay<sup>1</sup> professed to have prepared diamond in 1880, and Marsden,<sup>2</sup> in 1880-81, attempted to prepare it by dissolving carbon in molten silver, and obtained small crystals which may have been diamond.

Moissan,<sup>3</sup> who determined to repeat the experiments of Hannay, made a careful study of the allotropic forms of carbon, of their modes of formation and transformation, and of their physical and chemical distinctions.

The three following criteria must be obeyed before a substance can be pronounced to be diamond:

(i) Hardness; (ii) density; (iii) combustion figures.

(i) Other substances prepared in the electric furnace, *e.g.* boride of carbon, carbosilicide of titanium, are almost or quite as hard as diamond.

(ii) Density (3.5) is insufficient to characterise diamond; some substances prepared in the electric furnace, *e.g.* metallic borides and silicides, are as dense as or denser than diamond.

(iii) Carbon boride and some metallic carboborides burn producing carbon dioxide, but only carbon itself can produce 3.6 times its weight of carbon dioxide.

These three criteria taken together prove a substance to be diamond.

Moissan recognised that diamonds seldom, if ever, are found adhering to a matrix; and a study of "blue ground" from the Cape and of diamantiferous sand from Brazil proved that native microscopic diamonds are both black and transparent, and always accompanied by graphite. From "blue ground" Moissan isolated bort, carbonado, transparent diamond, and graphite. A study of a meteorite found in the Diablo Cañon, Arizona, furnished, however, the key to the problem. In the middle of a metallic mass were found "two small, transparent diamonds, of rough and grained surface, surrounded by amorphous carbon in distinctly compressed strips." This discovery impelled Moissan to experiment on the solution of carbon in metals at high temperature; and for this purpose he first adapted the electric furnace. In this furnace he dissolved carbon in silver, iron, aluminium, chromium, chromium, manganese, nickel, cobalt, tungsten, molybdenum, uranium, zirconium, vanadium, thorium, titanium, platinum, silicon. He obtained carborundum and many metallic carbides, but no diamond; carbon always separated from solution in metals as graphite.

Since graphite is the form of carbon stable at high temperature under ordinary pressure, Moissan next tried the effect of great pressure. Geological considerations favoured the view that diamond is formed by crystallisation from molten iron under high pressure. The occurrence of the diamonds in the centre of the Diablo Cañon meteorite, and in alluvial deposits as perfect crystals, suggested that terrestrial diamond may have been formed by crystallisation from molten iron under great

<sup>1</sup> Hannay, *Proc. Roy. Soc.*, 1880, 30, 188, 450.

<sup>2</sup> Marsden, *Proc. Roy. Soc.*, 1880-81, 11, 20, 37.

<sup>3</sup> See *The Electric Furnace*, by H. Moissan, Eng. edn., 1901, from which the information in this section is taken.

pressure in the depths of the earth. In order to test this opinion Moissan carried out the following experiments :

(i) Two hundred grammes of Swedish iron were covered with sugar-charcoal in a graphite crucible, heated to 3000° C. in the electric furnace, and then plunged beneath water to cool the molten metal suddenly. The iron of the regulus was dissolved in hydrochloric acid, and there remained three kinds of carbon: (a) graphite, (b) convoluted strips, as in Diablo Cañon meteoric iron, and (c) several greyish-black particles which were proved to be diamond.

(ii) Better results were obtained by cooling the molten iron, saturated with carbon, in molten lead, because no layer of steam retarded cooling and external solidification.

(iii) A further improvement consisted in packing a cylinder of soft iron with sugar-charcoal, strongly compressing the charcoal by means of a screw stopper of the same metal, and then immersing the cylinder in molten iron which was contained in a crucible and had been heated in the electric furnace for a few minutes. After the introduction of the cylinder the crucible was at once removed from the furnace and rapidly cooled.

The success of the experiment depends on rapid cooling, because iron, like water, expands on solidifying, and so the external crust exerts an enormous pressure inwards upon the core, which is rich in carbon.

By this means partially or wholly transparent diamonds were obtained which satisfied the most rigorous criteria. The largest, however, were not more than 0.6 mm. in diameter.

In his researches Moissan obtained transparent diamond crystallised in regular octahedra and cubes, irregularly crystallised fragments, crystals which split into fragments on keeping, like Prince Rupert's drops, and carbonado.

That diamond has been formed by crystallisation of carbon from a solvent, probably metallic, at high temperature and under great pressure, thus appeared to be established by Moissan.

Von Bolton,<sup>1</sup> however, has shown that crystalline particles of diamond dust act as nuclei for the deposition of carbon in the form of diamond from the hydrocarbons in coal-gas.

The observation that diamonds occur in fissures associated with nodules containing sulphur, silicon, and phosphorus led Moissan<sup>2</sup> to try the effect of adding these elements to the molten iron from which the diamond was to crystallise. Sulphur improved the yield; silicon also improved the yield, but the quality of the diamonds was poorer; phosphorus had an altogether unfavourable influence.

Moissan's final conclusions may thus be summarised: diamond is carbon which has been liquefied under high pressure; carbon heated to high temperature under atmospheric pressure vaporises without liquefying and yields a sublimate of graphite.

Moissan's conclusion as to the influence of high pressure in the formation of diamond has been substantiated by an observation of W. Crookes.<sup>3</sup> Crookes has examined the residues from the experiments of A. Noble on the explosion of cordite in closed cylinders. These

<sup>1</sup> Von Bolton, *Zeitsch. Elektrochem.*, 1911, 17, 971.

<sup>2</sup> Moissan, *Ann. Chim. Phys.*, 1905, [viii], 5, 174.

<sup>3</sup> Crookes, *Proc. Roy. Soc.*, 1905, A, 76, 458.

residues, produced under high temperature and high pressure occurring simultaneously, were found to contain diamonds.

C. V. Burton,<sup>1</sup> however, maintains that if carbon can be crystallised at comparatively low temperatures, the minimum pressure required to produce diamond will be lower than that employed by Moissan, and in some tentative experiments in which carbon was dissolved in a molten alloy of lead with about 1 per cent. of calcium, diamond appears to have been produced between 550° C. and 700° C. under atmospheric pressure when steam was passed over the alloy so as to react with and eliminate the calcium. Burton<sup>2</sup> also seems to have produced diamond by heating benzene or toluene with carbon tetrachloride or chloroform in a bomb to 200°–300° C. In this reaction carbon is separated, whilst hydrogen chloride accumulates under great pressure.

Further, as a result of attempts to melt carbon by electrical resistance heating under high pressure, which failed to yield more than a suspicion of diamond, C. A. Parsons<sup>3</sup> concludes that mechanical pressure is not the cause of the production of diamond in rapidly cooled iron containing carbon. Van Deventer<sup>4</sup> has endorsed Moissan's views from a theoretical standpoint.

**Uses of the Diamond.** Besides its value as a gem, diamond is employed for various special purposes on account of its great hardness. Bort was first used on the lapidary's wheel by La von Berquen of Bruges in 1476. It is employed in this manner not only for "cutting" diamonds, but also for faceting other precious stones.

A familiar use of diamond is for cutting glass. For this purpose a diamond must be mounted so that a curved edge between two adjacent facets is employed. This will cut more deeply into the glass than a straight edge, which may be used, however, for writing on glass. Diamonds are also used for drilling glass and porcelain, and for engraving and finishing metal-work, as well as for rock-drilling, which is their most important industrial application. For this purpose carbonado is preferred because it has no tendency to cleavage.

Diamonds are also used for the bearings in watches and electric meters, and, when drilled, for wire-drawing, on account of their great durability.

#### GRAPHITE

**History.** Graphite, like diamond, has been known from ancient times, and was early employed, as the word (*γράφω*, I write) indicates, for writing purposes. It was formerly, however, confused with molybdenum sulphide,  $\text{MoS}_2$ , which resembles it in appearance and in leaving a mark upon paper. The name *plumbago*, or *black lead*, shows that graphite was also identified with or thought to contain lead. Scheele, in 1779, distinguished clearly between molybdenum sulphide and graphite, showing the latter to be a mineral form of carbon since it is converted into carbon dioxide by nitric acid; and in 1800 Mackenzie showed that graphite burns like charcoal, producing carbon dioxide.

**Occurrence.** Graphite occurs in nodules in granite, gneiss, slate, and other rocks, in flakes or powder scattered throughout limestone, and sometimes in large masses. Excellent graphite was formerly found

<sup>1</sup> Burton, *Nature*, 1905, 72, 397.

<sup>2</sup> *Ibid*

<sup>3</sup> Parsons, *Proc. Roy. Soc.*, 1907, A, 79, 782.

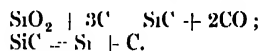
<sup>4</sup> Van Deventer, *Chem. Weekblad*, 1907, 4, 211.

at Seathwaite-in-Borrowdale, Cumberland, and made into lead-pencils at Keswick; but now these mines appear to be exhausted. Graphite is also found in Ceylon, in various parts of the United States, especially California, at Passau in Germany, and in Spain, Bohemia, Moravia, Styria, and Siberia (Irkutsk). Much of the graphite used in the United Kingdom comes from Ceylon; but Bohemian graphite is said to be the best for making pencils, and Ceylon graphite for the manufacture of crucibles. Graphite from these various sources varies much in purity. Passau graphite, for example, contains only about 13 per cent. of carbon, and Styrian graphite about 73 per cent., the remainder being in each case ash with a little volatile matter.

**Origin and Formation.**—Graphite is generally of organic origin, having being formed from carbonaceous material, probably without previous separation of amorphous carbon,<sup>1</sup> by pressure of overlying rocks and a sufficiently high temperature. The presence of about 1 per cent. of hydrogen<sup>2</sup> in natural graphite confirms this view of its formation.

Graphite is the most stable form of carbon at high temperatures. Thus the tips of the carbon electrodes of the arc lamp gradually become covered with a growth of graphite by vapourisation; and all kinds of carbon are vapourised, and thus converted into graphite, in the electric furnace. Likewise diamond is changed into graphite when placed between the poles of an electric arc. It has been shown by Arsen,<sup>3</sup> however, that other forms of carbon are not always converted into graphite when heated in closed crucibles to 3000°–3300° C. When various carbon compounds are decomposed at high temperature the carbon remains as graphite; graphite also results from the decomposition of carbides, cyanogen, acetylene, and carbon disulphide in the electric furnace.

Graphite of exceptional purity is prepared artificially by the Acheson process, by passing an electric current between carbon electrodes in a furnace built of fire-bricks and lined with carborundum. The intervening space is filled with sand and coke or anthracite. It is found that petroleum-coke yields a fine quality of graphite. The carborundum first formed decomposes, the silicon being volatilised and the carbon left in the form of graphite. Thus:



This graphite leaves on combustion only 0.05 per cent. of ash.

When carbon crystallises from molten metals, such as iron, it separates as graphite. This fact was first observed by Scheele in 1778. Whilst some of the carbon forms carbide, the excess is held in a state of solution from which it crystallises when the metal cools. Grey cast-iron contains more or less crystallised graphite; and graphite likewise occurs in meteoric iron. It has already been pointed out that when carbon crystallises from molten iron under great pressure it appears as diamond.

**Physical Properties.**—Graphite is grey and lead-like in appearance; it possesses a metallic lustre, and is opaque even in the thinnest flakes.

<sup>1</sup> Heimsch, *Monatsh.*, 1911, 32, 225.

<sup>2</sup> Regnault, *Ann. Chim. Phys.*, 1841, [iii], 1, 202.

<sup>3</sup> Arsen, *Trans. Amer. Electrochem. Soc.*, 1911, 28, 105.

It crystallises naturally and from molten iron, in hexagonal plates belonging to the monoclinic system. It is greasy to the touch, and its hardness on Moh's scale is less than 1, that of diamond being 10. It is on account of its softness, and because it rubs off in little scales, that it leaves a streak on paper; and it is the same property that makes it useful as a lubricant. Indeed, according to Threlfall,<sup>1</sup> it behaves under compression like a liquid. It is porous to gases.<sup>2</sup>

**Density.**—Since natural graphite is not a pure chemical substance, and is derived from different sources, its density is variable, but probably lies between the extreme values 2.015 and 2.583.<sup>3</sup> Rammelsberg<sup>4</sup> gave the value 2.17 to 2.32; Moissan<sup>5</sup> found the value for artificial graphite to lie between 2.0 and 2.25. Dewar<sup>6</sup> found that the density of an artificial graphite which was 2.099 at 17° C. became 2.1302 at the temperature of liquid air. According to Stromtz<sup>7</sup> the density of strongly compressed graphite may rise as high as 3.0. Arsen<sup>8</sup> would define graphite by its density: 2.25 to 2.26.

The coefficient of linear expansion of graphite between 190° C. and +17° C. is 0.0000241.<sup>9</sup> Fizeau,<sup>10</sup> however, found for natural graphite the values 0.00000786 at 10° C. and 0.00000796 at 50° C. The compressibility of graphite between 100 and 500 atmospheres is  $3 \times 10^{-6}$  vol./atm.<sup>11</sup>

**Specific Heat.**—The specific heat of graphite, like that of other non-metals, increases with temperature, but becomes approximately constant in the neighbourhood of 1000° C., and then gives a value for the atomic heat = 5.6.

The following results were obtained by H. F. Weber<sup>12</sup>:

Temp. °C.	Specific Heat	Atomic Heat	Temp. °C.	Specific Heat	Atomic Heat
— 50°	0.114	1.37	202°	0.297	3.56
— 10.7	0.111	1.73	249°	0.325	3.90
+ 10.8	0.160	1.93	612°	0.415	5.33
61.3	0.199	2.39	822°	0.454	5.45
138°	0.252	3.03	977°	0.467	5.60

Behn<sup>13</sup> has extended the values to lower temperatures, and gives the following interpolation formula:

$$C = 0.161 + 0.000628t - 0.000000112t^2.$$

<sup>1</sup> Threlfall, *Trans. Chem. Soc.*, 1908, 93, 1333.

<sup>2</sup> Graham, *Ann. Chem. Phys.*, 1864, [iv], 1, 110, 2, 151.

<sup>3</sup> Roscoe and Schorlemmer, *A Treatise on Chemistry* (Macmillan and Co.), 1911, vol. 1, p. 745.

<sup>4</sup> Rammelsberg, *Ber.*, 1873, 6, 188.

<sup>5</sup> Moissan, *The Electric Furnace* (Arnold) 1904, p. 77.

<sup>6</sup> Dewar, *Chem. News*, 1902, 85, 289.

<sup>7</sup> Stromtz, *Ann. Physik.*, 1900, [iv], 3, 1.

<sup>8</sup> Arsen, *Trans. Amer. Electrochem. Soc.*, 1911, 20, 105.

<sup>9</sup> Dewar, *Proc. Roy. Soc.*, 1902, 70, 247. See also Day and Sosman, *J. Ind. Eng. Chem.*, 1912, 4, 490.

<sup>10</sup> Fizeau, *Pogg. Annalen*, 1869, 138, 26.

<sup>11</sup> T. W. Richards, *Zeit. physikal. Chem.*, 1907, 61, 112.

<sup>12</sup> Weber, *Ber.*, 1872, 5, 303, *Pogg. Annalen*, 1875, 154, 367. See this series, vol. i, p. 90.

<sup>13</sup> Behn, *Drude's Annalen*, 1900, 1, 264.

Values calculated from this formula agree with Weber's results; but Dewar<sup>1</sup> has obtained the following smaller values at low temperatures:

Temperature interval	Specific Heat.
18° to - 78° C. . . . .	0.1311
18° to - 188° C. . . . .	0.0918
- 78° to - 188° C. . . . .	0.0599
- 188° to - 252.5° C. . . . .	0.0133

*Conductivity for Heat and Electricity* In contradistinction to diamond graphite is a good conductor of heat and electricity. Specimens from different localities vary, however, in their conductivity.<sup>2</sup> The following formula expresses the thermal conductivity of graphite<sup>3</sup>:

$$K = 0.0384 - 9 \times 10^{-5}t + 9.3 \times 10^{-7}t^2.$$

**Chemical Properties.** *Combustion.* When artificial graphite is heated in oxygen it begins to form carbon dioxide at 570° C., and the rate of formation increases up to 690° C., when inflammation occurs.<sup>4</sup> With natural graphite the temperatures at which these changes take place are variable, but they are considerably below the corresponding temperatures for diamond (*q.v.*); and this difference constitutes one of the distinguishing tests between the two forms of carbon.

*Action of Oxidising Agents* Graphite differs much from diamond in its reactivity towards liquid oxidising agents. Cold, concentrated nitric acid has no action on graphite; but some specimens, when strongly heated after being moistened with the acid, intumescce, *i.e.* swell up, because of the generation of gas within them. The gas consists of carbon dioxide and oxides of nitrogen, and is probably produced by the action of the acid on particles of amorphous carbon contained within the graphite.<sup>5</sup> Luza distinguishes between different kinds of graphite by this reaction of intumescence.<sup>6</sup> Specimens that intumescce are known as "graphite," those which do not as "graphitite." The variety from Ceylon is "graphite," that from Borrowdale "graphitite." The artificial product is generally "graphitite." When molten cast-iron containing carbon is cooled by water the external layers contain graphitite, the interior graphite; intumescent graphite is, moreover, produced by dissolving carbon in molten platinum, and remains when the platinum is removed by aqua regia.

Graphite is slowly oxidised when heated with a mixture of nitric and sulphuric acids, or potassium chlorate with sulphuric or nitric acid. These reactions, which were discovered by Brodie,<sup>7</sup> may be used for the purification of graphite or its conversion into "graphitic acid."<sup>8</sup> If graphite is heated with a mixture of 1 part of nitric acid and 4 parts of sulphuric acid, or 14 parts of graphite are heated with 1 part of

<sup>1</sup> Dewar, *Proc. Roy. Soc.*, 1905, **A**, 76, 236. See also Dewar, *Phil. Mag.*, 1872, [iv], 44, 461; Kunz, *Ann. Chem. Phys.*, 1903, **14**, 327; Voille, *Compt. rend.*, 1895, **120**, 868.

<sup>2</sup> Muraoka, *Bull. London*, 1881, **13**, 307; Artom, *Atti Acc. Torino*, 1902, **37**, 475; Piesch, *Wien. Ber.*, 1893, [v], 102, 768.

<sup>3</sup> Icote, *Ann. Chem. Phys.*, 1912, [viii], 25, 137.

<sup>4</sup> Moissan, *Compt. rend.*, 1902, **135**, 921.

<sup>5</sup> Moissan, *ibid.*, 1893, **116**, 608. See also Threlfall, *Trans. Chem. Soc.*, 1908, **93**, 1333; and Ostwald, *Grundriss der anorganischen Chemie*, 1900, 390.

<sup>6</sup> Luza, *Ber.*, 1891, **24**, 4085; 1892, **25**, 216, 1378; 1893, **26**, 890.

<sup>7</sup> Brodie, *Ann. Chem. Phys.*, 1855, [iii], 45, 351; *ibid.*, 1860, [iii], 59, 466.

potassium chlorate and 28 parts of sulphuric acid, the graphite is partially oxidised and turns violet, but regains its black colour when washed with water. When strongly heated the mass swells up, loses gases, and yields a residue of pure graphite of density 2.25.

Mixtures of concentrated sulphuric acid and potassium permanganate or chromic acid may be substituted for Brodie's mixture.<sup>1</sup>

By more prolonged treatment with similar reagents graphite is converted into graphitic acid.

For this purpose one part of graphite and 3 parts of potassium chlorate are mixed with nitric acid and heated for several days at 60° C., and after washing the process is repeated four or five times. On the powdered graphite may be mixed with sulphuric and nitric acids at the ordinary temperature and a large excess of potassium chlorate be added. A green product results, which is changed into graphitic acid by treatment with potassium permanganate and sulphuric acid.<sup>2</sup>

Graphitic acid is yellow, and appears to be crystalline because it preserves the form of the original graphite crystals. Its composition corresponds to the formula  $C_{11}H_7O_6$  or  $C_{11}H_5O_6$ , but it is really an amorphous mixture of several compounds of high molecular weight.<sup>3</sup> When the acid is heated it decomposes explosively, evolving carbon monoxide, carbon dioxide, and water, and leaves a black, charcoal-like residue called pyrographitic acid, which is converted by potassium chlorate and nitric acid into mellitic acid,  $C_6(COOH)_6$ .

Graphitic acid is reduced by stannous chloride to a black "pseudo-morph" which resembles graphite in appearance, and may be oxidised again to graphitic acid.

The behaviour of graphite towards oxidising agents, by which graphitic acid is produced, distinguishes this substance from diamond and from amorphous carbon, for diamond is not acted upon by these reagents, and amorphous carbon is dissolved by them with the formation of humic and finally mellitic acid. According to Charpy, however, some forms of carbon hitherto regarded as amorphous, such as carbon from steel and the product obtained by heating graphitic acid, yield graphitic acid on oxidation. It therefore appears unsatisfactory to define graphite with reference to the action of oxidising agents.<sup>4</sup>

**Uses of Graphite.** The usefulness of graphite depends upon its peculiar softness and sealiness, as well as upon its chemical inertness, infusibility, and conductivity for electricity. For the manufacture of black-lead pencils natural graphite itself was formerly used, being cut up into strips of the required size. Now, however, powdered graphite is mixed into a paste with fine clay, and the mixture is pressed through a hole so as to form a thread.

Graphite crucibles are made from a mixture of powdered graphite and fine clay. They are moulded like pottery and then fired. They are employed for melting metals, and especially in the manufacture of crucible steel. (See vol. ix.)

A well-known application of graphite is for protecting non-*e.g.* grates - from rust. It is also used in electrotyping, the surface on which electrodeposition of metal is to take place being covered with a layer of graphite, which is a conductor.

<sup>1</sup> Charpy, *Compt. rend.*, 1909, 148, 920

<sup>2</sup> Staudenmaier, *Ber.* 1898, 31, 1181, 1899, 32, 1394, 2824

<sup>3</sup> Staudenmaier, *Ber.* 1899, 32, 2832

<sup>4</sup> Charpy, *Compt. rend.*, 1909, 148, 920



It is likewise employed as a lubricant for machinery, and as a coating for gunpowder to prevent absorption of moisture. The efficiency of the powder is, however, somewhat diminished by the graphite.

#### AMORPHOUS CARBON

Amorphous carbon, as usually met with, contains a variable proportion of impurity derived from the organic compounds or natural products from which it is prepared. Sugar-charcoal, lampblack, soot, gas-carbon, vegetable and animal charcoal, and coke are reckoned as forms of amorphous carbon. The impurities present within them may be "organic," *i.e.* may consist of compounds of hydrogen, oxygen, and nitrogen, which ignition has failed to remove; or inorganic, which will remain as ash when the carbon has been burned away.

**Preparation of Amorphous Carbon.**—Amorphous carbon may be formed in a variety of ways, but its preparation in a state of purity is difficult. It is liberated in the following reactions:

(1) Decomposition of carbonaceous matter at high temperature (sugar, vegetable and animal charcoal, coke).

(2) Deposition from dissociated hydrocarbon vapours (lampblack, soot, gas-carbon).

(3) Explosive decomposition of endothermic compounds, *e.g.* acetylene.

(4) Deposition in electrolysis:

(a) at anode in electrolysis of silver acetylide;

(b) at cathode in electrolysis of concentrated sulphuric acid with carbon electrodes;

(c) at cathode in electrolysis of fused  $\text{BaCO}_3 + \text{BaCl}_2$  at  $600^\circ \text{C}$ .

(5) Reduction of CO and  $\text{CO}_2$  by metals:

*e.g.*  $\text{CO}_2$  by magnesium, calcium and the alkali metals, and CO by iron at high temperature.

(6) Decomposition of CO:

(a) by heat at  $1690^\circ \text{C}$ . into  $\text{CO}_2$  and free carbon<sup>1</sup>;

(b) by radium emanation into  $\text{O}_2$ ,  $\text{CO}_2$ , and carbon.<sup>2</sup>

Sugar-charcoal and lampblack yield the purest forms of amorphous carbon, because they need contain no mineral impurity.

**Sugar-Charcoal**, prepared by heating pure, white, ashless sugar, preferably in a platinum capsule, until combustion of volatile matter ceases, forms a black, shining, porous mass, which, however, contains "organic" impurities that cannot be eliminated by ignition alone. It is consequently heated in a current of dry chlorine at  $1000^\circ \text{C}$ . for several hours, then washed with hot water, and again ignited in dry hydrogen till hydrogen chloride ceases to be evolved.<sup>3</sup> The density of purified sugar-charcoal is 1.8, and its ignition temperature about  $450^\circ \text{C}$ .

**Lampblack and Soot.**—It is well known that the luminous flame of a candle or of coal-gas deposits carbon upon a cool surface brought in contact with it. This is because the combustion of carbon particles in the flame, whose incandescence is the cause of luminosity, is prevented by cooling.

If a flame is not properly ventilated it will smoke and deposit soot

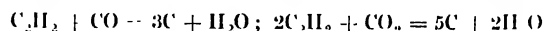
<sup>1</sup> Meyer and Langer, *Ber.*, 1885, 18, 131e

<sup>2</sup> Cameron and Rausav, *Trans. Chem. Soc.*, 1908, 93, 966.

<sup>3</sup> Bono and Jerdan, *Trans. Chem. Soc.*, 1897, 71, 45

without artificial cooling; and this is the more likely to happen if the proportion of carbon in the burning vapour is large. Thus the hydrocarbon vapours arising from coal burning in the grate smoke and deposit soot in the chimney, and hydrocarbons such as benzene vapour and acetylene burn with very smoky flames unless their combustion is carefully regulated.

Frank's process of obtaining soot consists in burning acetylene with carbon monoxide or dioxide according to the following reactions:



Lampblack is made by burning tar or resinous matter, or aromatic compounds such as naphthalene, in an insufficient supply of air, and collecting the smoke on cloths, metallic plates, or revolving cylinders. The lampblack is partially purified by being heated in closed vessels, but even then contains about 20 per cent. of oily impurities, which are removed by ignition in a current first of chlorine, then of hydrogen, as in the case of sugar-charcoal.

The density of lampblack is 1.78, but rises to 1.87 when the lampblack is heated for some hours at 910° C.; by the same treatment the ignition temperature rises from 371° to 476° C.

The finest quality of lampblack is used for making Indian ink, and in calico-printing; common lampblack is employed as the basis of printers' ink and black paint.

**Gas Carbon or Retort Carbon** is formed as a lining on the upper parts of the retorts in which coal is heated in the manufacture of coal-gas. It owes its origin to the thermal dissociation of the hydrocarbon vapours evolved from the coal; and the process may be copied by passing ethylene ( $\text{C}_2\text{H}_4$ ) through a red-hot porcelain tube, when gas carbon is formed. It contains little or no hydrogen and about 3 per cent. of ash; it is therefore a moderately pure form of amorphous carbon. Gas carbon is grey in colour and very hard; it approaches graphite in its density, which is over 2.0, and it is a good conductor of heat and electricity. On this account it is used, when ground together with charcoal and graphite, for making electric-light carbons and the carbon plates or rods of Bunsen batteries.

**Vegetable- or Wood-Charcoal** (*i.e.* turn-coal, from O.E. *char*, to turn; therefore wood turned to coal).—Charcoal-burning is an ancient process, and in countries where wood is plentiful it is still carried out as originally. Logs of wood are piled nearly vertically in a conical mound round a central shaft. The mound is covered with turf or moistened ashes; ventilating holes are left at the bottom. The pile is ignited by brands thrown down the shaft, and thick white smoke, consisting of the volatile products of combustion, escapes up the shaft during the process of burning, the latter being checked if necessary by stopping up the ventilating holes. When the combustion is finished the pile is carefully covered and left to cool for some days. After this the charcoal is removed, and further cooled, if necessary, by water thrown upon it. Sometimes, as in Austria and Sweden, fir logs are piled horizontally for charcoal-burning.

This process is evidently very wasteful, since all the volatile products are lost, except so far as their combustion within the pile helps to maintain its temperature. A process of destructive distillation in closed vessels was known to the alchemists, and is employed at the

present day. Wood in small pieces or sawdust is carbonised in cast-iron retorts, and the volatile products are collected. These consist of wood spirit or methyl alcohol, acetone, pyroigneous acid, which is impure acetic acid, and wood-tar or creosote.

The production of charcoal from wood may be compared with the formation of coal from carboniferous vegetation, the pressure of the superincumbent strata in coal-formation having a similar effect to high temperature. And just as there are different grades of coal, reaching a maximum carbon-content in anthracite, so there are different grades of charcoal, the percentage of carbon in which depends upon the temperature of carbonisation.

Wood begins to turn brown at about 220° C.,<sup>1</sup> at 280° C. it becomes deep brown, and at 310° C. black, soft, and friable; when prepared at high temperature charcoal is, however, brittle.

Stein<sup>2</sup> has traced the process of carbonisation by heating wood with water in sealed tubes between 245° C. and 290° C., with the following results:

Temp. ° C.	245	250	255	265	275	280	290
Per cent. Carbon	64.3	69.2	70.3	72.8	74.0	77.6	81.3
Hours heating	9	6	6	5	5	5	5

The amount of carbon in the product depends upon pressure as well as temperature; it never exceeded 78 per cent. under atmospheric pressure, even at red heat.

The following table<sup>3</sup> shows the composition of charcoal produced at different temperatures:

Temp. ° C.	270	350	432	1023	1100	1270	1300	1500	Over 1500
Carbon	70.45	76.64	81.64	81.97	83.29	88.14	90.81	94.57	96.51
Hydrogen	4.64	4.14	1.96	2.30	1.70	1.41	1.58	0.74	0.62
Oxygen with some nitrogen	21.06	18.61	15.21	14.13	13.79	9.25	6.46	3.03	0.93
Ash	0.85	0.61	1.16	1.60	1.22	1.20	1.15	1.66	1.91
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Thus by very strong ignition nearly, but not quite, all the hydrogen can be driven out of charcoal. Wood-charcoal ordinarily contains, however, from 85 to 90 per cent. of carbon and from 2 to 3 per cent. of hydrogen.

During carbonisation wood shrinks in volume as well as losing in weight. Thus 100 parts of wood yield about 65 parts of charcoal by measure and 25 parts by weight.

*Density of Charcoal.*—Since wood shrinks during carbonisation the density of charcoal is greater than that of the wood from which it has been produced. It varies according to the nature of the wood and the temperature of formation of the charcoal, but lies between 1.45 and 2.0. This value, however, applies to charcoal from the pores of which

<sup>1</sup> Percy, *Metallurgy Fuel*, p. 107.

<sup>2</sup> Stein, *Chem. Zentr.*, 1901, ii, 950, from *Magy. Chem. folyirat*, 6, 39.

<sup>3</sup> Roscoe and Schorlemmer, *A Treatise on Chemistry* (Macmillan & Co.) 1911, vol. i, p. 754.

air has been removed. The density of charcoal containing air in its pores varies from 0.1 to 0.2. The effect of removing air from the pores of charcoal may be shown by floating some fragments of charcoal on cold water and then boiling the water for some time. The air is thus driven out of the pores, and the charcoal eventually sinks in the water. The same effect may be produced by placing the charcoal and water in a flask from which the air is continuously pumped.

**Absorption of Gases by Charcoal** If a piece of freshly ignited wood-charcoal is introduced into a tube of ammonia gas standing over mercury, the gas is slowly taken up by the charcoal, so that the mercury rises in and may eventually fill the tube. A similar effect may be observed with hydrogen-sulphide gas. This phenomenon, which might simply be called absorption, is termed *adsorption*<sup>1</sup> because it is essentially a surface phenomenon. It is a general property of solid bodies to condense gases, vapours, and liquids upon their surfaces; this property renders difficult the washing of finely divided precipitates in gravimetric analysis.

The greater the specific surface of a solid the greater its power of adsorption. Now wood charcoal presents an exceedingly great surface by reason of its cellular structure, for the walls of every microscopic cell throughout its mass contribute to the superficial area; therefore, after the adsorbed air has been removed by ignition the charcoal is able to adsorb many times its own volume of another gas.

This phenomenon, which is connected with surface energy, was first observed in 1777 by Scheele and Fontana, but first investigated quantitatively by Saussure,<sup>2</sup> who found that the quantity of gas adsorbed by a solid depended on its properties and its pressure, but that Henry's law of gas-absorption does not apply.

The following results were obtained by Saussure. One volume of charcoal adsorbs the following volumes of various gases measured at 12° C. and 721 mm

Ammonia	90	Nitrous oxide	10	Oxygen	9.25
Hydrogen chloride	85	Carbon dioxide	35	Nitrogen	6.50
Sulphur dioxide	65	Ethylene	35	Hydrogen	1.25
Hydrogen sulphide	55	Carbon monoxide	9.42		

It will be observed not only that there is a great difference between the volumes of different gases adsorbed, but also that extent of adsorption is connected with condensibility.

Similar experiments were carried out by Hunter.<sup>3</sup>

Subsequent work of Chappuis,<sup>4</sup> Joulin,<sup>5</sup> and Kayser<sup>6</sup> enabled Ostwald<sup>7</sup> to deduce a law of adsorption which is expressed by the equation

$$c = ka^m$$

where  $c$  = concentration or pressure of the gas,  $a$  the amount adsorbed,

<sup>1</sup> See Ostwald, *Lehrbuch der allgemeinen Chemie*, 1903, i, pp. 1081-1098.

<sup>2</sup> Saussure, *Gilbert's Annalen*, 1814, 4<sup>th</sup>, 2, 113.

<sup>3</sup> Hunter, *Phil. Mag.*, 1861 [iv], 25, 364, 1865, 29, 116.

<sup>4</sup> Chappuis, *Wied. Annalen*, 1881, 12, 160.

<sup>5</sup> Joulin, *Ann. Chim. Phys.*, 1881, [v], 22, 397.

<sup>6</sup> Kayser, *Wied. Annalen*, 1881, 12, 526.

<sup>7</sup> Ostwald, *Lehrbuch der allgemeinen Chemie*, 1906, ii, 3, 232.

while  $k$  and  $m$  are constants which depend upon the nature and temperature of the gas.

Dewar<sup>1</sup> has shown that the volume of gas adsorbed increases greatly with lowering of temperature, as the following figures indicate :

	Vol at 0° C.	Vol at 185° C.
Hydrogen . . . . .	4	35
Nitrogen . . . . .	15	155
Oxygen . . . . .	18	230
Argon . . . . .	12	175
Helium . . . . .	2	15

This property is now utilised for separating the rare gases of the air; for charcoal cooled in liquid air will adsorb oxygen, argon, and nitrogen readily, but has much less influence on hydrogen, helium, neon, krypton, and xenon.<sup>2</sup> On the same account charcoal is employed for producing high vacua, since it adsorbs the last traces of gas from an enclosed space. Condensation takes place during adsorption, and therefore heat must be evolved in the process.

Favre<sup>3</sup> obtained the following results for the volumes of gases adsorbed by 1 c.c. of charcoal at ordinary temperature, and the heats of adsorption per gram of gas<sup>4</sup> :

Gas	Volume adsorbed	Heat of adsorption
	c.c.	calcs.
Ammonia . . . . .	178	191
Hydrogen chloride . . . . .	166	274
Hydrogen bromide . . . . .	—	191
Hydrogen iodide . . . . .	—	173
Sulphur dioxide . . . . .	165	168
Nitrous oxide . . . . .	99	169
Carbon dioxide . . . . .	97	158

Wood-charcoal also possesses the power of adsorbing colouring and other matters from solution, but in this property it is surpassed by animal charcoal, under which these phenomena will be described.

*Catalytic Influence of Charcoal.*—Not only does wood-charcoal adsorb various gases, but it also possesses the power of promoting chemical changes between them.

If, for example, some freshly ignited charcoal is immersed in hydrogen-sulphide gas, and subsequently in oxygen, combustion of the hydrogen

<sup>1</sup> Dewar, *Ann. Chim. Phys.*, 1904, [viii], 3, 5.

<sup>2</sup> See also Valentiner and Schmidt, *Drude's Annalen*, 1905, 18, 189. Wohl and Losanitsch, *Ber.*, 1905, 38, 4150. Miss Homfray, *Chem. News*, 1907, 96, 93.

<sup>3</sup> Favre, *Compt. rend.*, 1874, 39, 729; *Ann. Chim. Phys.*, 1874, [v], 1, 209.

<sup>4</sup> See also Miss Homfray, *Proc. Roy. Soc.*, 1910, A, 84, 99, and *Zeitsch. physikal. Chem.*, 1910, 74, 129, 687. Titoff, *ibid.*, 1910, 74, 641; Schmidt, *ibid.*, 1910, 74, 689. Beigter, *Ann. Physik*, 1912, [iv], 37, 472.

sulphide takes place within the pores of the charcoal and sufficient heat is developed to ignite the latter, which then burns brilliantly in the oxygen. It was, moreover, observed by Melsen<sup>1</sup> that when charcoal saturated with chlorine is brought into dry hydrogen formation of hydrogen chloride takes place even in the dark. Further, it was shown by Stenhouse<sup>2</sup> that charcoal not only absorbs obnoxious gases—as, for instance, from sewers—but also causes their oxidation by the atmosphere. On this account charcoal finds practical application as a deodorant<sup>3</sup>.

Thus wood-charcoal has the power of hastening chemical action between adsorbed gases; that is to say, it is a *catalyst*.

**Animal Charcoal.**—Animal charcoal is produced from bones, horn, blood, etc. *Bone-black*, or *bone-charcoal*, is obtained by the destructive distillation of bones in iron retorts, the distillate constituting bone-oil or Dippel's oil. Bone-black contains about 80 per cent. of calcium phosphate, a little calcium carbonate, some combined nitrogen, and only about 10 per cent. of carbon. The following is an analysis of a good sample of dried bone-black<sup>4</sup>:

Carbon . . . . .	10.51
Ca and Mg phosphates, $\text{CaF}_2$ , etc. . . . .	80.21
$\text{CaCO}_3$ . . . . .	8.30
$\text{CaSO}_4$ . . . . .	0.17
$\text{Fe}_2\text{O}_3$ . . . . .	0.12
$\text{SiO}_2$ . . . . .	0.34
Alkali salts . . . . .	0.35
	<hr/>
	100.00

The carbon is diffused in a very finely divided state throughout the mineral skeleton, and consequently presents a very large surface which possesses adsorptive properties.

Blood-charcoal is made by evaporating blood with potassium carbonate, igniting, washing the charred residue with water and hydrochloric acid, and again igniting. The potassium carbonate furnishes a basis on which the carbonaceous matter is deposited and rendered porous.

An artificial form of charcoal, which simulates animal charcoal in porosity and adsorptive power, may be obtained by mixing sugar with bone-ash and igniting the mixture.

The special characteristic of animal charcoal, on which its use depends, is its power to remove substances from solution. For example, it is well known that a brown solution of raw sugar is decolorised when boiled with animal charcoal. Other substances that are similarly removed from solution are indigo, litmus, iodine, the colouring-matter of red wine, the brown matter of peaty water or sewage, astringent principles, and certain basic salts, as well as fusel oil from alcohol. It is upon this property that the use of animal charcoal for filtering water depends, and also its employment in the laboratory for purifying organic compounds by removing the tarry matter which is frequently

<sup>1</sup> Melsen, *Compt. rend.*, 1893, 76, 81, 92.

<sup>2</sup> Stenhouse, "On Charcoal as a Disinfectant," *Proc. Roy. Inst.*, 1855, 2, 53, *Pharm. J.*, 1856, 16, 363.

<sup>3</sup> Thorpe, *Dictionary of Applied Chemistry* (Longmans & Co.), 1912, vol. i, p. 265.

formed with them. Animal charcoal is also employed technically for purifying paraffin and glycerine, and its dust for making ivory-black and blacking. When the power of the charcoal is exhausted it may be renewed by ignition or treatment with reagents.

All these phenomena are further examples of adsorption, which includes the fixation by solids of liquids or substances in solution<sup>1</sup> as well as of gases.

It is chiefly substances of large molecular weight, especially colloidal substances, which are adsorbed from solution by charcoal.<sup>2</sup>

From a study of the decolorising action of various forms of charcoal Knecht<sup>3</sup> supports the view that animal charcoal owes its decolorising action to the presence within it of organic compounds stable at red heat.

The theory of adsorption has been developed by Freundlich<sup>4</sup> and Löwe,<sup>5</sup> whose conclusions, however, have been criticised by McBain.<sup>6</sup> The process of adsorption of iodine by various forms of charcoal has been investigated by Davis,<sup>7</sup> who has reached the following conclusions:

(1) Adsorption of iodine by charcoal consists of a surface condensation and a diffusion (solid solution) into the interior of the carbon.

(2) Surface condensation is rapid, and complete in some hours; diffusion continues for weeks or months.

(3) Surface condensation is independent of diffusion.

(4) Sugar and animal carbons possess, roughly, the same power of adsorption; coco-nut carbon is much less efficient and its action is chiefly due to diffusion.

(5) The amount of adsorption is specific and depends on the nature both of the solvent and of the adsorbing substance.

The adsorption of phenol, benzoic acid, and picric acid from alcoholic solutions by carbon has been studied by Gustafson,<sup>7</sup> who finds that the adsorption of picric acid takes place in accordance with the theory of Freundlich.

**Coke.**—Coke is the residue produced by heating coal out of contact with air till all volatile matter has been removed; it is thus a by-product in the manufacture of coal-gas. Coke is often made also by burning coal in covered heaps after the fashion of charcoal-burning, or by heating it in special coke-ovens. Coke made in ovens is hard, lustrous, and dense, prismatic in structure, silvery-grey and metallic-looking; it is a good conductor of heat and electricity, and difficult to burn. When made by burning coal in heaps coke is dull black, spongy, and easily combustible.

The chief use of coke is for the smelting of iron in the blast-furnace; but for this purpose only the hard coke made in ovens can be employed.

**Physical Properties of Amorphous Carbon.**—*Specific Heat.* Like that of diamond and graphite, the specific heat of amorphous carbon is variable and increases with temperature. In accordance, however,

<sup>1</sup> For the theory of adsorption of dissolved substances, see S. Lagergren, *Zeitsch. physikal. Chem.*, 1900, **32**, 174.

<sup>2</sup> Knecht, *Seventh Intern. Congr. Appl. Chem.*, 1909, Sect. IV, n, 17.

<sup>3</sup> Freundlich, *Zeitsch. physikal. Chem.*, 1907, **57**, 385.

<sup>4</sup> Freundlich and Löwe, *Zeitsch. physikal. Chem.*, 1907, **59**, 281.

<sup>5</sup> McBain, *Trans. Chem. Soc.*, 1907, **91**, 1683.

<sup>6</sup> Davis, *Trans. Chem. Soc.*, 1907, **91**, 1666.

<sup>7</sup> Gustafson, *Zeitsch. Elektrochem.*, 1915, **21**, 159.

with its lower density the specific heat of amorphous carbon is greater at corresponding temperature than that of graphite or diamond. The following results were obtained by Wigand<sup>1</sup>:

	Density	Specific Heat	Temperature °C.
Diamond	3.518	0.1128	10.7
Graphite	2.25	0.1601	10.8
Gas-carbon	1.885	0.2010	21.68

Earlier investigations on the specific heat of amorphous carbon were made by Regnault<sup>2</sup> (from 1810), Bettendorff and Wulher<sup>3</sup> (1868), and Weber<sup>4</sup> (1875). Dewar<sup>5</sup> obtained the value 0.3115 for gas-carbon for the temperature interval 20–1010°, and Kunz<sup>6</sup> has measured the specific heat of wood-charcoal at various temperatures and calculated the following interpolation formula, which applies to all temperatures between 100° and 1300°:

$$S = 0.2113 + 0.1136 \times 10^{-4} + 0.1975 \times 10^{-7} T^2$$

**Conductivity for Heat and Electricity.** The conductivity for heat of gas-carbon, which is fifteen times as great as that of coal is 0.0103, i.e. the amount of heat that passes in one second from one surface to the other of a uniform plate of 1 sq. cm. area and 1 cm. thick, there being 1° C. temperature difference between the two surfaces, would heat 0.0103 gram of water 1° C.

The electric conductivity of gas-carbon resembles that of graphite; its value<sup>7</sup> at 0° C. is  $0.0115 \times 10^4$ . Von Strömte<sup>8</sup> has investigated the electric conductivity of compressed Lampblack, and found that it increases with rising temperature between 77° C. and 12° C., like that of an electrolyte, but Dewar and Fleming<sup>9</sup> have shown that the conductivity of electric-light filaments below the temperature of liquid air (–182°) is similar to that of metals, i.e. it decreases with rising temperature. The conductivities of electric-light filaments are, according to Dewar and Fleming<sup>9</sup>:

at 182° C.	0.0235	$10^4$
„ – 100° C.	0.0241	$10^4$
„ 18.9° C.	0.0252	$10^4$

It has been found by Moore<sup>10</sup> that the thermoelectric properties of amorphous carbon vary with temperature, and depend on the raw material used and its treatment. Consequently it is inferred that amorphous carbon is not a single, definite substance.

**Chemical Properties of Amorphous Carbon.** In accordance with its less density and the absence of crystalline form, amorphous carbon is more susceptible to oxidation by chemical reagents than graphite or diamond. A mixture of hot concentrated nitric acid and potassium

<sup>1</sup> Wigand, *Annalen Physik*, 1906, [iv], 22, 61–98.

<sup>2</sup> Regnault, *Ann. Chim. Phys.*, 1840, [iii], 73, 5; 1840, [iv], 129.

<sup>3</sup> Wulher, *Pogg. Annalen*, 1868, 133, 1.

<sup>4</sup> Weber, *Pogg. Annalen*, 1875, 154, 367.

<sup>5</sup> Dewar, *Phil. Mag.*, 1872, [iv], 44, 461.

<sup>6</sup> Kunz, *Drude's Annalen*, 1903, 14, 327.

<sup>7</sup> Siemens, *Wied. Annalen*, 1880, 10, 560.

<sup>8</sup> Strömte, *Ann. Physik*, 1900, [iv], 3, 1.

<sup>9</sup> Dewar and Fleming, *Phil. Mag.*, 1892, [v], 34, 326.

<sup>10</sup> Moore, *J. Amer. Chem. Soc.*, 1915, 37, 2032.



chlorate, which has no action on diamond and converts graphite into graphitic acid, more or less readily dissolves amorphous carbon, converting it into humic and mellitic acids. This reaction, which serves to distinguish between the different allotropic forms of carbon, is known as Brodie's reaction.<sup>1</sup>

Sugar-charcoal, wood-charcoal, lignite, coal, anthracite, and soot are acted upon when heated with concentrated nitric acid alone, giving brown solutions; coke- and gas-carbon do not colour the acid. A mixture of concentrated nitric and sulphuric acids dissolves all forms of amorphous carbon; but coke is the most resistant towards this reagent. Lignite and coal are oxidised to oxalic acid by alkaline permanganate solution; and alkali hypobromite dissolves lignite.

Amorphous carbon is oxidised to carbon dioxide when heated with sulphuric acid and potassium dichromate, or with molten potassium chlorate or nitrate; it combines with hydrogen under certain conditions to form  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$  (*q.v.*), and with sulphur vapour, forming  $\text{CS}_2$ . Carbon also combines at high temperatures with metals, such as Fe, Ni, Co, to form carbides—as, for instance, in the cementation and case-hardening processes for steel—and reacts with lime in the electric furnace to form calcium carbide (*q.v.*)

*Amorphous Carbon as a Reducing Agent.*—Besides being used as a fuel, amorphous carbon, in one form or another, finds application as a reducing agent. The "blowpipe reactions on charcoal," familiar to every student of qualitative analysis, exemplify the use of carbon as a reducing agent. In these reactions metallic oxides, such as those of silver, bismuth, copper, lead, tin, are reduced to the metallic state.

The use of coke in the blast-furnace, of anthracite in the reduction of tin and zinc ores, the process of "poling" in copper-smelting, are examples of reduction by carbon in metallurgy. The carbon anodes employed in the electrometallurgy of aluminium are consumed in the process, and no doubt their material aids the reduction of the alumina by combining with its oxygen. The preparation of phosphorus also involves the reduction of phosphate by charcoal or coke.

*Combustion of Carbon.*—When carbon burns in excess of air or oxygen the product consists of carbon dioxide only; when, however, carbon dioxide comes in contact with glowing carbon it is reduced to carbon monoxide. It is an interesting question whether CO is first formed by the direct combustion of carbon or whether the product of combustion of carbon is at once and only  $\text{CO}_2$ .

Lang<sup>2</sup> believed that all the CO formed when oxygen was passed over gas-carbon at 500° owed its origin to the reduction of  $\text{CO}_2$ , but Dixon<sup>3</sup> pointed out that Lang's experimental results did not preclude the formation of CO previous to  $\text{CO}_2$ ; and, moreover, that  $\text{CO}_2$  is not reduced to CO below 600°. H. B. Baker's<sup>4</sup> experiments appear to show that carbon burns in two stages, and that when thoroughly dried carbon and oxygen combine the chief product is CO. C. J. Baker<sup>5</sup> found that dry carbon which had adsorbed dry oxygen at 12° C. gave off a gas at 150° C. which was mainly CO. Dixon<sup>6</sup> has shown that CO is

<sup>1</sup> Brodie, *Phil. Trans.*, 1859, 149, 249.

<sup>2</sup> Lang, *Zeitsch. physikal. Chem.* 1888, 2, 168.

<sup>3</sup> Dixon, *Trans. Chem. Soc.*, 1899, 75, 630.

<sup>4</sup> H. B. Baker, *Phil. Trans.*, 1888, A, 179, 571.

<sup>5</sup> C. J. Baker, *Trans. Chem. Soc.*, 1887, 57, 249.

<sup>6</sup> Dixon, Strange, and Graham, *Trans. Chem. Soc.*, 1896, 59, 769.

formed before  $\text{CO}_2$  in the combustion of cyanogen, *i.e.* of gaseous carbon. Finally Rhead and Wheeler<sup>1</sup> have proved from a consideration of the relative rates of the various reactions between oxygen,  $\text{CO}$ ,  $\text{CO}_2$ , and carbon that in the burning of carbon the two oxides are produced simultaneously, and they<sup>2</sup> are of opinion that the oxygen first enters the carbon molecule, oxygenating it by forming an unstable physico-chemical complex,  $\text{C}_x\text{O}_y$ , and that the energy of this combination causes some of the oxygen molecules to detach some of the carbon atoms and depart with them as molecules of carbon dioxide, whilst other oxygen molecules are "torn apart in the process" become atomised, and leave the carbon molecule as carbon monoxide."

**Heat of Combustion of Carbon, and Relations between the Different Allotropic Forms.** Small differences have been observed between the heats of combustion of the different allotropic forms of carbon. The following values were obtained by Favre and Silbermann<sup>3</sup> for the reaction  $[\text{C}, \text{O}_2]$ , *i.e.* for the combustion of 12 grams of carbon to 44 grams of carbon dioxide:

Diamond (1)	93,210 calories.
" (2)	91,650 "
Natural graphite	93,560 "
Cast-non graphite	93,110 "
Wood-charcoal	96,960 "

The heat of the reaction  $[\text{C}, \text{O}]$  was found to be 29,000 calories.

The following figures were obtained by Berthelot<sup>4</sup>

Diamond	Graphite	Amorphous Carbon.
91,310 calories	91,810 calories <sup>5</sup>	97,650 calories.

whence the following heats of formation are calculated<sup>6</sup>:

Diamond from amorphous carbon	3310 calories.
Graphite "	2810 "
Diamond from graphite	500 "

According to Mixer,<sup>7</sup> the carbon obtained by the decomposition of acetylene is to be regarded as a distinct allotropic form, whose heat of combustion is 91,730 calories, whilst that of sugar-charcoal is 96,680 calories, and of graphite 93,970 calories. The density of this form is 1.919, and Moissan has shown that it is not identical with graphite.

From a consideration of the above thermal differences between diamond, graphite, and amorphous carbon it appears that the formation of graphite from diamond is an endothermic reaction, and that diamond contains less internal energy than the other forms of carbon, and is therefore probably the most stable modification at ordinary temperatures.

From a study of equilibrium in the systems  $\text{C}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{Fe}$ ,  $\text{FeO}$ ,  $\text{CO}$ ,  $\text{CO}_2$  Schenck and Heller<sup>8</sup> conclude that between  $100^\circ\text{C}$  and  $800^\circ\text{C}$ , graphite is the most stable and charcoal the least stable form of carbon.

<sup>1</sup> Rhead and Wheeler, *Trans. Chem. Soc.*, 1912, 101, 831, 846

<sup>2</sup> Rhead and Wheeler, *ibid.*, 1913, 103, 461

<sup>3</sup> Favre and Silbermann, *Ann. Chem. Phys.*, 1852 [m], 34, 414

<sup>4</sup> Berthelot, *Compt. rend.*, 1889, 108, 1144

<sup>5</sup> Roth and Wallasch (*Ber.*, 1913, 46, 896) have found the heat of combustion of graphite to be 94,218 calories

<sup>6</sup> Berthelot and Petit, *Ann. Chem. Phys.*, 1889, [vi], 18, 80

<sup>7</sup> Mixer, *Amer. J. Sci.*, 1905, 19, 434

<sup>8</sup> Schenck and Heller, *Ber.*, 1905, 38, 2139. see also *Ber.*, 1907, 40, 1704, and A. Smits, *Ber.*, 1905, 38, 4027

These considerations have an important bearing on the reduction of iron in the blast-furnace. Faleke,<sup>1</sup> however, throws doubt on Schenck's conclusions.

Roozeboom points out<sup>2</sup> that from 3000° C., at which temperature diamond is converted into graphite, down to about 1000° C., when graphite is still the most stable form of carbon, diamond is in a metastable condition (Fig. 1). No transition-point is known, however, between

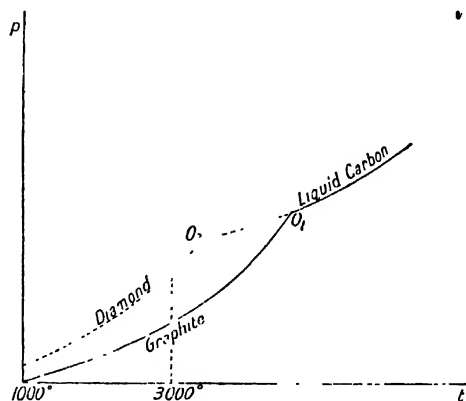


FIG. 1. Physical states of carbon. (After Roozeboom.)

graphite and diamond; therefore it appears uncertain which is the more stable form at atmospheric temperature. Nevertheless, by Nernst's theorem<sup>3</sup> the transition temperature is calculated to be 372° C., below which temperature diamond would be the most stable form of carbon. It has further been calculated that graphite is converted into diamond at the temperature of molten iron under a pressure of about 10,000 atmospheres.<sup>4</sup>

**Fusion and Vaporisation of Carbon.** Carbon vapourises in the electric arc under atmospheric pressure at about 3600° C., and condenses as graphite. Moissan<sup>5</sup> has shown that when carbon is heated in an electric furnace in a carbon tube at 2000 amperes and 80 volts it vaporises, and the tube is filled with a light deposit, which by chemical tests is proved to be graphite. Moissan was of opinion that carbon vapour always yields graphite by condensation, but according to Berthelot<sup>6</sup> the film deposited on the glass of carbon filament electric lamps is amorphous carbon. Moissan concluded, moreover, that carbon might be liquidised under great pressure; and showed that diamonds having the appearance of congealed drops, besides occurring naturally, might

<sup>1</sup> Faleke, *Ber.*, 1913, 46, 713. See vol. ix (this series).

<sup>2</sup> Roozeboom, *Physikalische*, 1901, p. 179.

<sup>3</sup> Nernst, *Sitzungsber. K. Akad. Wiss.*, Berlin, 1906, p. 935, and *Chem. Zentr.*, 1906, ii, 397.

<sup>4</sup> Cf. Moissan's work on diamond, this vol., p. 35.

<sup>5</sup> Moissan, *Compt. rend.*, 1894, 119, 776; see also *The Electric Furnace*, by Henri Moissan, Eng. trans., 1904, p. 110 et seq.

<sup>6</sup> Berthelot, *Compt. rend.*, 1903, 137, 589.

be prepared artificially under great pressure. That carbon powder cannot be welded by great pressure alone was shown by Spring.<sup>1</sup>

In a study of the thermal effects of the musical arc, La Rosa<sup>2</sup> has obtained evidence of the fission of carbon and of its crystallisation in particles which sink in bromoform and methylene iodide and scratch ruby.

The physical constants of carbon have been calculated by Crookes<sup>3</sup> in the following manner:

The critical temperature of a substance is about 1.5 times its boiling or vapourising temperature at atmospheric pressure. The vapourising temperature of carbon is about 3870° abs (= 3600° C); therefore its critical temperature is about 5800° abs. Further, the critical temperature of a substance is numerically equal to about 2.5 times its critical pressure; so that the critical pressure of carbon is about 2320 atmospheres.

Lastly, the melting-points of substances that sublime (e.g. arsenic) are about 1.1-1.2 times as high as their vapourising temperatures at atmospheric pressure; consequently the lowest melting point of carbon is about 4400°. By the application of the Rankine-van der Waals equation  $\log P = 10.11 \frac{39,210}{T^2}$ , the pressure corresponding to this melting-point is found to be about 16 atmospheres. Thus the following physical constants of carbon have been arrived at:

Temp. (abs.)	Press. (atm.)	
3870°	1	vaporisation-point
4400°	16	melting-point
5800°	2320	critical point

## PROPERTIES OF CARBON

	Diamond	Graphite	Amorphous carbon
Crystalline form	Octahedral and cubes (cubic system)	Hexagonal plates (monoclinic system)	
Hardness	10	1	Variable
Density	3.52	About 2.2	1.1-1.9
Refractive index for sodium light	2.417		
Coefficient of linear expansion	0.0000012	0.0000079	
Specific heat at atmospheric temperature	0.1128	0.1604	0.2040
Conductivity for heat	Good	Good	0.0103 K
" " electricity	Bad	Good	0.0145 - 10 <sup>10</sup> at 0° (gas carbon)
Combustion			
Evolution CO <sub>2</sub> begins	720° C	570° C	500° C
" " vigorous	790° C	600° C	
Inflammation temperature	800-850° C	690° C	315° C
Action of KClO <sub>3</sub> + HNO <sub>3</sub>	None	Forms graphitic acid (insol.)	Forms humic acid (sol.)

<sup>1</sup> Spring, *Ann. Chim. Phys.*, 1881, [v], 22, 170

<sup>2</sup> La Rosa, *Compt. rend.*, 1909, 148, 475-616

<sup>3</sup> Crookes, *Proc. Roy. Soc.*, 1905, A, 76, 458

## COAL

Coal is the name given to various kinds of carboniferous material of vegetable origin found in the crust of the earth. Vegetable matter—peat, lignite, soft coal, anthracite—forms a series of fuels which show a regular gradation in properties, though the plants which produced peat and lignite were not of the same nature as those that gave rise to true coal. Chemically, the transformation of vegetable remains into coal has consisted in the loss of volatile matter, and the consequent increase in the proportion of carbon. This fact is illustrated by analyses, thus :

	Carbon	Hydrogen	Oxygen and Nitrogen
Wood . . . . .	49.76	6.14	44.80
Sphagnum, chief plant of peat-bogs . . . . .	19.88	6.54	43.58
Black peat . . . . .	59.70	5.70	34.60
Lignite from Tenditz, Germany . . . . .	57.02	5.91	37.04
Lignite from Sardina . . . . .	82.26	6.52	11.22
Non-caking bituminous coal, S. Staffordshire . . . . .	81.39	5.73	12.87
Bituminous coal, Pennsylvania . . . . .	85.73	5.19	8.78
Cannel coal, Wigan . . . . .	83.58	5.77	10.65
Fossil plants from coal-beds, Commeny, France . . . . .	82.45	1.75	12.80
Welsh anthracite . . . . .	92.73	3.37	3.90
Ural anthracite . . . . .	97.16	0.61	1.93

It is noteworthy that in the course of transformation of vegetable matter into coal the diminution of hydrogen is small compared with that of oxygen and nitrogen. This fact is of great economic importance.

**Peat.**—Peat is produced from plants which grow in bogs, especially bog-moss or sphagnum. Below the surface of the bog the vegetable structure gradually gives place to a black, somewhat gelatinous mass of peat, which is cut into blocks, dried, and used as fuel. Heather, grasses, sedges, and trees may give rise to peat; occasionally the remains of trees, such as bog-oak and bog-pine, of an ebony-black colour, are found embedded in peat.

Peat consists essentially of water, inorganic matter, vegetable fibre, and humus. It is produced from vegetable matter, probably through the action of micro-organisms, with gradually increasing pressure of superincumbent material. Thus a bed originally a foot thick may be compressed to three inches; and if peat is buried beneath drift or clay the pressure upon it may be further increased, and conditions set up which would eventually transform peat into a kind of coal.

**Lignite.**—Lignite, or brown coal, is intermediate in composition between peat and coal. It is rightly called fossil wood, for it consists of the remains of trees and shrubs of the Tertiary epoch, which closely resembled those of to-day. It cannot be regarded as coal in

process of formation, since the latter is not derived from wood; and it differs from coal in being easily acted on by nitric acid. It is variable in composition, hardness, and colour. Jet is a very hard variety of lignite, which is probably derived from coniferous wood.

**Origin of Coal.** A study of the relationships of the carboniferous to other strata, and of the fossils found in the coal measures, makes possible a fairly accurate view of the origin and mode of formation of coal. Coal-bearing strata occur first in the later primary rocks of the earth's crust, and occur in various subsequent formations. The flora and fauna existing when true coal was formed were very different from those of the present day. The vegetation of the coal period, as shown by fossil remains, was chiefly cryptogamic, consisting of giant tree-ferns, reeds, equisetæ, and club mosses, but conifers and cycads also occurred, and then seeds, together with the spores of lycopods, contributed in large part to the coal. Forest trees, however, such as oak and elm, had not yet appeared.

All this vegetation flourished exceedingly in marshy land and in an atmosphere rich in carbon-dioxide gas. Dead and decaying vegetation was buried beneath succeeding layers of similar material, or of sediment which hardened into rock, thus under enormous and ever-increasing pressure, by the agency of bacteria but in the absence of air, layers of coal were gradually formed.

Various attempts have been made to imitate artificially the processes by which coal has come into existence, by submitting carbonaceous material to high pressure and temperature. Spring<sup>1</sup> submitted peat to 6000 atmospheres pressure, and converted it into a hard, black, shining substance like coal. Violette<sup>2</sup> heated wood to nearly 400° C. in a sealed tube; the volatile products exerted a great pressure, and the solid remaining had the appearance of a fatty coal. Cagniard de la Tour<sup>3</sup> performed similar experiments, and Fremy<sup>4</sup> heated carbohydrates and "ulmic acid" in sealed tubes to about 300° C. and obtained the following coal-like products, which yielded water, gas, tar, and coke by destructive distillation.

COMPOSITION OF ARTIFICIAL COALS

	Carbon	Hydrogen	Oxygen
Coal from sugar	66.81	1.78	28.43
" " starch	68.48	1.68	26.84
" " gum arabic	78.78	5.00	16.22
" " ulmic acid (peat)	76.06	1.99	18.95
" " " (vasculose)	78.78	5.31	18.26

S. Stein<sup>5</sup> has carried out experiments with wood heated with water in sealed tubes, to which reference has been made under charcoal.

<sup>1</sup> Spring, *Bull. Acad. Roy. Belg.*, 1880, 49, 367.

<sup>2</sup> Violette, *Ann. Chim. Phys.*, 1851, [3], 32, 304.

<sup>3</sup> Cagniard de la Tour, *Compt. rend.*, 1831, 32, 295.

<sup>4</sup> Fremy, *Compt. rend.*, 1879, 88, 1048.

<sup>5</sup> Stein, *Chem. Zentr.*, 1901, u, 1950.

More recently Bergius<sup>1</sup> has heated peat, cellulose, and water to a temperature of 340° C. for eight hours at a pressure of 100 atmospheres, and has thus obtained a finely divided black powder, very similar to ordinary coal so far as its composition and qualitative reactions are concerned. Subsequent heating to above 300° C. under pressure of about 5000 atmospheres yielded a coherent mass resembling coal in its physical properties.

**Chemical Constitution of Coal.** Little was known until recently about the chemical constitution of coal. Considerable light, however, has been thrown upon this difficult problem by the work of Wheeler and his collaborators, to which reference will shortly be made. First of all it may be said that the number and complexity of the products of the destructive distillation of coal in the manufacture of coal-gas throw little light upon the constitution of coal itself, because these products may have been formed or altered in the process of distillation, and the proportion between them certainly varies with varying conditions of treatment. That coal cannot properly be described as an allotropic form of carbon may be judged from the fact that it is not certain that every kind of coal contains free carbon at all. Probably lignite contains no free carbon, but anthracite undoubtedly contains it. Caustic soda, potash, and ammonia extract humic acid from peat and lignite, but not from true coal. When lignite is fused with caustic soda pyrocatechin is obtained. True coals do not yield this compound.

The investigations of Wheeler<sup>2</sup> and others were commenced with a view to elucidate the causes and conditions of the explosions of mixtures of coal-gas and air in mines.

It has been shown by these observers that in the careful destructive distillation of coal different volatile products are obtained at different temperatures. Ethane, propane, butane, and higher members of the series of paraffin hydrocarbons form a large percentage of the gases evolved below 150° C. The evolution of these gases ceases, however, above 700° C., and hydrogen and oxides of carbon take their place, so that the composition of the evolved gases shows a marked change at 750°–800° C., a "critical period" lying between these temperatures. It is inferred from these phenomena that "coal contains two types of compounds of different degrees of ease of decomposition—the one, the more unstable, yielding the paraffin hydrocarbons and no hydrogen; the other, decomposed with greater difficulty, yielding hydrogen alone (or, possibly, hydrogen and the oxides of carbon) as its gaseous decomposition product."

Another mode of attack was to treat the coal with various solvents. This had been done before, such solvents as petroleum-ether, benzene, and alcohol having been used. Pyridine,<sup>3</sup> moreover, had been found to be a valuable solvent, which now yielded important results. Pyridine extracts from coal that portion of it which gives rise to the paraffin hydrocarbons on destructive distillation, together with some of the hydrogen-yielding portion. Re-extraction of the pyridine extract with chloroform or benzene gives the paraffin-yielding fraction fairly pure.

<sup>1</sup> Bergius, *J. Soc. Chem. Ind.*, 1913, 32, 462

<sup>2</sup> Burgess and Wheeler, *Trans. Chem. Soc.*, 1910, 97, 1917, 1911, 99, 649. Clark and Wheeler, *Trans. Chem. Soc.*, 1913, 103, 1701. Wheeler, *Trans. Chem. Soc.*, 1913, 103, 1715. Burgess and Wheeler, *Trans. Chem. Soc.*, 1914, 105, 131. Jones and Wheeler, *Trans. Chem. Soc.*, 1914, 105, 140, 1916, 109, 707.

<sup>3</sup> T. Baker, *Trans. Inst. Min. Eng.*, 1900, 20, 159. P. P. Bedson, *J. Soc. Chem. Ind.*, 1908, 27, 147. Donath, *Chem. Zeit.*, 1908, 32, 1271.

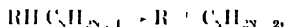
This product is of a resinous nature, whilst the portion insoluble in chloroform is a degradation-product of cellulose, *i.e.* a humus substance. The "humus substances," whether left in the coal after extraction with pyridine or as a residue after chloroform or benzene re-extraction, were found to yield on distillation mainly phenols, whilst the "resinous substances" yielded no phenols, but olefines and naphthenes, as well as paraffins.<sup>1</sup>

These products are the remains respectively of the resinous constituents and woody fibre of a "monster vegetation which flourished long before the earth was inhabited by man."<sup>2</sup>

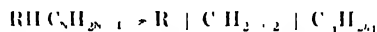
The distillation of bituminous coal in a vacuum at temperatures not exceeding 430° C. yielded further information<sup>3</sup> with regard to the resinous substances, and further extraction of the pyridine-chloroform extract with pentane yielded crystals of paraffin wax of melting-point 55–59° C., which formed about 0.1 per cent. of the original coal. These results have led to the formulation of a theory with regard to the compounds in coal itself which yield volatile hydrocarbons by distillation at low temperature.

Liquid or gaseous paraffins cannot have been produced by the thermal decomposition of free solid paraffins, which are not present in sufficient quantity, and neither can it be thought that they are formed by pyrogenic synthesis under the conditions of the experiments. It is believed that they are present in the coal substance combined somewhat loosely with a less volatile residue from which they are liberated by moderate heat.

The distillation of "free" paraffins from "bound" molecules is thus represented



or



A similar explanation is applied to the breaking down of ethylene and naphthalene molecules.<sup>4</sup>

From a thermal study of the process of carbonisation of coal and related substances Hollings and Cobb<sup>5</sup> arrive at the following conclusions:

(1) Below 400° C. cellulose shows a strongly exothermic reaction beginning at 345° C., and probably due to loss of hydroxyl groups, and consequent molecular condensation. Coal itself does not show this reaction.

(2) 400°–600° C. is the temperature interval in which the characteristic differences in different types of coal are exhibited. Oils, unsaturated hydrocarbons, higher paraffins, and oxygenated compounds are evolved, the thermal phenomena varying with the quality of the coal.

(3) 600°–800° C. is the temperature interval in which methane is evolved, and all coals are exothermic. If the carbonisation process is on the whole exothermic, the thermal reaction at this stage is the predominant cause.

(4) Above 800° C. hydrogen is the chief product, and the change is thermally neutral, or slightly endothermic.

<sup>1</sup> Jones and Wheeler, *Trans. Chem. Soc.*, 1914, 105, 2562, 1915, 107, 1418.

<sup>2</sup> Lewes, *The Carbonisation of Coal*, London, 1912, p. 21.

<sup>3</sup> Similar experiments have been carried out by Pictet and Bouvier (*Compt. rend.*, 1913, 157, 779).

<sup>4</sup> Jones and Wheeler, *Trans. Chem. Soc.*, 1914, 105, 140.

<sup>5</sup> Hollings and Cobb, *Trans. Chem. Soc.*, 1915, 107, 1106.



**Varieties of Coal.**—True coal is divided into two classes: bituminous coal and anthracite.

*Bituminous coal* varies considerably in composition, but burns always with a luminous and smoky flame, and yields by destructive distillation in closed retorts hydrogen and volatile hydrocarbons, which compose coal-gas, ammonia, water, and tar or bitumen.

Two varieties of bituminous coal are caking and non-caking coal. Caking coal undergoes incipient fusion during burning, becoming pasty, and yielding a variety of coke which is cellular and dissimilar in form from the coal. Non-caking coal shows no signs of fusion when burnt, and does not yield a true coke.

Cannel (candle) coal, also called parrot coal, is a highly bituminous kind of coal which takes fire when held in a flame. It is dull black, and shows no banded structure, but has a conchoidal fracture. It is often rich in nitrogen, which is derived from the remains of fish<sup>1</sup> embedded in the coal when it was being laid down under water.

ANALYSES OF BITUMINOUS COALS

	Non-caking		Caking		Cannel	
	A	B	C	D	E	F
Carbon . . .	75.81	87.62	81.41	78.69	80.07	78.06
Hydrogen . . .	5.22	4.34	5.83	6.00	5.53	5.80
Oxygen . . .	11.14	2.52	7.90	10.07	8.08	3.12
Nitrogen . . .	1.93	1.13	2.05	2.37	2.12	1.85
Sulphur . . .	0.90	1.07	0.74	1.51	1.50	2.22
Ash . . .	5.00	3.32	2.07	1.36	2.70	8.95

A. St Helens, Lancashire    B. Dowlas, South Wales    C and D. Northumberland  
E. Wigan    F. Tyneside

*Anthracite*, produced from vegetable matter by loss of the maximum amount of volatile constituents, is hard, black, and metallic-looking. It burns without smoke, gives a maximum heat of combustion, and is used for steam-raising.

ANALYSES OF ANTHRACITE

	South Wales	Pennsylvania
Carbon . . .	90.39	92.59
Hydrogen . . .	3.28	2.63
Oxygen . . .	2.98	1.61
Nitrogen . . .	0.83	0.92
Sulphur . . .	0.91	—
Ash . . .	1.61	2.25

<sup>1</sup> Newberry, *Amer. J. Sci.*, 1854, ii 23, 212. Rofe, *Geol. Mag.*, 1860, p. 208

**Precarboniferous coals**, such as anthraxolite, schungite, and graphitoid, contain an even less proportion of volatile matter than anthracite. They are metamorphic coals, but contain their carbon in the amorphous state.

**The Gases in Coal.** It is not necessary for coal to be heated in order to give off gas. Much gas is occluded or adsorbed in coal, or is pent up in cavities in the seams. This gas is chiefly methane, and, because it is the cause of fires and explosions in mines, it is called fire-damp. Owing to the physical condition of the gas in the coal, its rate of evolution is influenced by variations in atmospheric pressure. Hence miners are warned that a sudden fall in the barometer indicates danger from explosion of fire-damp. The occurrence of methane in coal is connected with the vegetable origin of the latter. Just as marsh-gas is generated by vegetable matter decaying under water at the present day, so was it produced from the plants of the carboniferous period. No doubt much of this gas escaped, but some remained adsorbed within the structure of the coal in process of formation. It is particularly in deep mines, and therefore where coal is under great pressure, that fire-damp occurs.

The composition of the gas which can be extracted from coal by heating it to 100° C. *in vacuo* has been investigated by Thomas<sup>1</sup>. The following are representative analyses of the gas from 100 grams of coal:

	Bituminous Coal	Steam Coal	Anthracite
Volume of gas	55.1 c.c.	117.4 c.c.	600.6 c.c.
Percentage of CO <sub>2</sub>	5.44	18.90	11.72
“ CH <sub>4</sub>	63.76	67.47	84.18
“ O <sub>2</sub>	1.05	1.02	—
“ N <sub>2</sub>	29.75	12.61	1.10

The greater volume of gas obtained from anthracite is due to the fact that, being less porous than bituminous coal, it retains its gas better than the latter during removal from the mine.

The gases in coal have been investigated by Trobridge.<sup>2</sup>

#### ATOMIC WEIGHT OF CARBON

In his original table of atomic weights, published in 1803, Dalton gave 4.3 as the atomic weight of carbon, but altered this in 1808 to 5. Prout, in 1815, wrote C = 6, and Gmelin attributed the same value to the equivalent of carbon. Thénard, in 1826, accepted for the atomic weight C = 12.25 (H = 1), Messner, in 1834, C = 12.1 (H = 1); Kuhn, in 1837, C = 6.1 (H = 1).

This confusion was removed by the recognition of Avogadro's theory, and the fact that never less than 12 parts by weight of carbon are present in a molecular proportion of any of its volatile compounds;

<sup>1</sup> Thomas, *Trans. Chem. Soc.*, 1876, 28, 793.

<sup>2</sup> Trobridge, *J. Soc. Chem. Ind.*, 1906, 25, 1120.

though Wanklyn,<sup>1</sup> in 1894, unsuccessfully attempted to revive the value  $C = 6$ , on the ground that Russian kerosene contained hydrocarbons in whose molecules there would appear to be present half-atoms of carbon, e.g.  $C_{11}H_{12}$ , if the atomic weight of carbon were made equal to 12.

Although the specific heat of carbon varies for the different allotropes, and also varies in the case of each allotrope with temperature, it approaches a constant value, which is the same for diamond and graphite, at about 600° C. Thence, if  $C = 12$ , the atomic heat of carbon becomes 5.5, a value comparable with that of analogous elements (see vol. i (this series), p. 90).

In the Periodic Table there is a vacancy for an element exhibiting the same general properties as carbon, the atomic weight of which lies between those of boron (11.0) and nitrogen (14.01).

The methods employed in the accurate determination of the atomic weight of carbon have been many and varied, but they all fall into one of two categories, namely, (1) *physical methods*, based upon determining the densities of gaseous compounds, and (2) *chemical methods*, depending upon the combustion of carbon or the analysis of its compounds.

(1) **Physical Methods.** On the assumption that Avogadro's theory is rigidly true, and therefore that oxygen and carbon monoxide undergo no change of volume when they are separately converted into carbon dioxide, the molecular weights of these three gases can be compared by determining their densities: so that the atomic weight of carbon can be calculated if that of oxygen is known.

Wollaston,<sup>2</sup> in 1814, first calculated the atomic weight of carbon in this manner from the density determinations of Biot and Arago, namely:

Density of oxygen (air = 1)	= 1.10339
Density of carbon dioxide	= 1.51961

Hence, atomic weight of carbon ( $O = 16.00$ ) = 12.063

Berzelius and Dulong,<sup>3</sup> in 1819, obtained the following values:

Density of oxygen (air = 1)	= 1.1026
Density of carbon dioxide	= 1.5215

Hence, atomic weight of carbon ( $O = 16.00$ ) = 12.24.

They confirmed this value for the atomic weight of carbon by a chemical method (*vide infra*).

On the authority of Berzelius this value was accepted for a number of years, though R. D. Thomson,<sup>4</sup> in 1836, obtained the figure  $C = 12.000$  by a density determination. Wrede,<sup>5</sup> however, in 1842, subsequently to the chemical methods of Liebig and Redtenbacher in 1841, pointed out that carbon dioxide is more compressible at ordinary temperatures than corresponds with Boyle's law, and that oxygen therefore yields less than its own volume of carbon dioxide, the density of which is correspondingly high. He estimated the ideal density of carbon dioxide to be 1.52037, that of oxygen 1.1052, and that of carbon monoxide

<sup>1</sup> Wanklyn, *B. I. Reports*, 1894; *Chem. News*, 1894, 70, 89.

<sup>2</sup> Wollaston, *Phil. Trans.*, 1814, 104, 20.

<sup>3</sup> Berzelius and Dulong, *Ann. Chim. Phys.*, 1819, 15, 392.

<sup>4</sup> Thomson, *Records of General Science*, 1836, p. 179.

<sup>5</sup> Wiede, *Jahresber.*, 1842, 22, 72.

0.96779; whence by comparison of densities he obtained the following results:

From the ratio CO, CO, atomic weight of C	12.023
" " CO O " C	12.021
" " CO + O " C	12.022

the mean value being  $C = 12.022$  ( $O = 16$ ).

The above results, however, are merely of historical interest.

Modern investigators have, like Wiede, recognised the approximate character of Avogadro's theory and devised methods whereby gaseous densities may be utilised for the determination of exact molecular weights. Of these methods, D. Berthelot's "method of limiting densities" and Guye's "method of critical constants" have been explained in vol. I of this series. Leduc has devised a third method, the "method of molecular volumes," which is in principle identical with that of Berthelot although the actual methods of calculation adopted by Leduc are somewhat different. Leduc<sup>1</sup> has determined the densities of carbon monoxide, carbon dioxide, acetylene and oxygen at N.T.P. relatively to that of air, and also measured the compressibilities of these gases. His density results when that of oxygen is unity, are as follows:

$$CO = 0.87195; CO_2 = 1.38324; C_2H_2 = 0.8194$$

the values for the oxides of carbon being in excellent agreement with Lord Rayleigh's data for the same gases. Leduc's method of calculation leads to the following results:

Molecular weight of CO	28.005, whence atomic weight of C	12.005
" " CO <sub>2</sub>	44.005, " "	C = 12.005
" " C <sub>2</sub> H <sub>2</sub>	26.026 " "	C = 12.005

where  $O = 16$  and  $H = 1.00762$ , and the same method of calculation gives for methane the results. Molecular weight of  $CH_4 = 16.036$ , whence atomic weight of  $C = 12.006$  when Baume and Perrot's value<sup>2</sup> for the weight of a "normal" litre of the gas is adopted, viz. 0.71680 grammes.

D. Berthelot, in 1898, calculating by his method and utilising for the purpose the experimental data of Leduc and Rayleigh, arrived at the value  $C = 12.005$ , as the most probable mean of a number of values ranging from 12.000 to 12.007.<sup>3</sup> Berthelot's method, however, cannot be very satisfactorily applied to gaseous carbon compounds, since their compressibilities at  $0^\circ C$ . have not been directly measured, and attempts to calculate them from either van der Waals' equation or one of its modifications are not very satisfactory.<sup>4</sup> The above cited value for the density of methane, together with Leduc's determinations of the compressibility at  $16^\circ C$ ., give

Molecular weight of  $CH_4 = 16.039$ , whence atomic weight of  $C = 12.0085$  while Rayleigh's value<sup>5</sup> for the density of carbon monoxide at N.T.P.,

<sup>1</sup> Leduc, *Ann. Chim. Phys.*, 1898, [vi], 15, 5; 1910, [viii], 19, 111.

<sup>2</sup> Baume and Perrot, *J. Chim. phys.*, 1900, 7, 369.

<sup>3</sup> D. Berthelot, *Compt. rend.*, 1898, 126, 951, 1020, 1115-1501; *J. Physique*, 1899, [iii], 8, 263; see also *Zeitsch. Elektrochem.*, 1901, 10, 621; *Compt. rend.*, 1907, 144, 76, 194, 269, 352; 145, 317.

<sup>4</sup> See vol. I (this series), chap. IV.

<sup>5</sup> Rayleigh, *Proc. Roy. Soc.*, 1897, 62, 204; 1901, 73, 153; *Phil. Trans.*, 1904, A, 204, 351; *Zeitsch. physikal. Chem.*, 1905, 52, 705.

viz. 0.87497 ( $O = 1$ ), and his value for the compressibility at about  $13^{\circ} \text{C.}$ , lead to

Molecular weight of  $\text{CO} = 28.003$ , whence atomic weight of  $\text{C} = 12.003$ .

Guye's method of critical constants<sup>1</sup> may be applied to the difficultly liquefiable gases carbon monoxide and methane. The density of carbon monoxide at N.T.P. is 0.87497 according to Rayleigh, and 0.87495 according to Leduc, when that of oxygen is unity. The mean value corresponds to a weight of 1.25032 grams for a normal litre of carbon monoxide. A similar volume of methane, according to Baume and Perrot, weighs 0.71680 grams. Guye's method of calculation leads to the following results:

Molecular weight of  $\text{CO} = 28.003$ , whence the atomic weight of  $\text{C} = 12.003$   
 " "  $\text{CH}_4 = 16.034$ , " " " "  $\text{C} = 12.004$   
 $O = 16$ ,  $H = 1.00762$ .

In dealing with readily liquefiable gases Guye adopts carbon dioxide as the standard from which to derive the constants in his formulae, and assumes an atomic weight of  $\text{C} = 12.002$ . Accordingly, the values  $\text{C} = 12.001$  and  $\text{C} = 12.003$ , that may then be derived from the densities of acetylene<sup>2</sup> and ethane<sup>3</sup> respectively, only serve to indicate the consistency of the method of calculation.<sup>4</sup>

(2) **Chemical Methods.** From an analysis of purified naphthalene, Dumas,<sup>5</sup> in 1838, came to the conclusion that the value for the atomic weight of carbon ( $\text{C} = 12.21$ ) obtained by Berzelius and Dulong in 1819, by the density method previously referred to, was too high. Consequently Berzelius<sup>6</sup> analysed lead carbonate and oxalate, converting them to monoxide, and obtained the value  $\text{C} = 12.212$ , which appeared to justify his previous result. Dumas, however, was unconvinced, and, together with Stas, carried out a series of researches to determine the ratio  $\text{C} : \text{CO}_2$  by the combustion of diamond and natural and artificial graphite.

The graphite employed was purified by fusion with alkali, followed by treatment with hydrochloric acid and with aqua regia, and subsequently, after washing and drying, by ignition at a white heat for sixteen to eighteen hours in a stream of chlorine. The graphite or diamond was contained in a platinum boat placed in a porcelain tube and heated in a furnace, and was burnt in a current of carefully purified oxygen, the carbon dioxide being absorbed in potash bulbs. Both graphite and diamond left a minute ash, the weight of which was subtracted from that of the substance taken.

It has been pointed out by Scott<sup>7</sup> that in correcting their weighings for the air displacement of the potash solution, Dumas and Stas, as well as later experimenters, neglected to take account of the expansion

<sup>1</sup> Guye, *Compt. rend.*, 1904, 138, 1213; *J. Chim. phys.*, 1905, 3, 321.

<sup>2</sup> Guye, *loc. cit.*

<sup>3</sup> Baume and Perrot, *J. Chim. phys.*, 1909, 7, 369. The value 12.036 given in the original paper is due to an arithmetical error.

<sup>4</sup> For further work on the atomic weight of carbon, by physical methods, see Baume, *J. Chim. phys.*, 1908, 6, 1; Jaquero and Perrot, *Compt. rend.*, 1905, 140, 1542.

<sup>5</sup> Dumas, *Pogg. Annalen*, 1838, 44, 110.

<sup>6</sup> Berzelius, *Lib. Annalen*, 1841, 38, 195.

<sup>7</sup> Scott, *Trans. Chem. Soc.*, 1897, 71, 550.

# CARBON AND ITS COMPOUNDS

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of this solution during its absorption of carbon dioxide. Consequently the values obtained by these observers are slightly too high.

Mean value obtained by Dumas and Stas . . . C 11.9975  
 " " corrected by Scott C 11.9938

Erdmann and Marchand<sup>1</sup> carried out experiments similar to those of Dumas and Stas, weighing the carbon dioxide produced in the combustion of diamond and graphite. They made, however, the same omission as the former experimenters, and their result, together with the correction of Scott, was as follows:

Uncorrected. Corrected by Scott.  
 C 12.0093 12.0051

Later experiments of a similar kind to which the same correction needed to be applied were those of Roseoe,<sup>2</sup> Friedel<sup>3</sup> and van der Plaats.<sup>4</sup>

	Uncorrected	Corrected by Scott
Roseoe . . . . .	12.0029	11.9973
Friedel . . . . .	12.0112	12.0056
Van der Plaats . . . . .	12.0031	12.0018

The mean of the five values obtained by the above observers from the combustion of carbon, after correction by Scott, gave C = 12.0008.

Stas,<sup>5</sup> in 1849, estimated the atomic weight of carbon by passing carbon monoxide over heated copper oxide, and determining the loss in weight of the latter and the weight of carbon dioxide formed. From the relation  $O_2 : CO_2$  thus found the value C = 12.0016 ( $O = 16$ ) may be obtained. Scott<sup>6</sup> has critically examined the above method, and finds it vitiated by a number of experimental errors which have evidently compensated each other to yield this accurate figure.

Another method for determining the atomic weight of carbon which must be noticed is that depending on the ignition of organic silver salts.

Lachg and Redtenbacher,<sup>7</sup> in 1841, obtained the following results from the ignition of (a) silver acetate, (b) silver tartrate, (c) silver racemate, (d) silver malate

(a) $C_2H_3O_2Ag$ Ag = 100.616065, whence atomic weight of C	12.039
(b) $C_4H_4O_6Ag_2$ 2 Ag = 100.592806, " " " C	12.044
(c) $C_4H_4O_6Ag_2$ 2 Ag = 100.592769, " " " C	12.049
(d) $C_4H_4O_6Ag_2$ 2 Ag = 100.620016, " " " C	12.050

Marignac,<sup>8</sup> in 1846 found

$C_2H_3O_2Ag$ Ag = 100.61609, whence atomic weight of C	12.035, and
$C_2H_3O_2Ag$ Ag = 100.64619, " " " C	11.986;

the latter result following special precautions against loss of silver by

<sup>1</sup> Erdmann and Marchand, *J. prakt. Chem.*, 1841, 23, 159

<sup>2</sup> Roseoe, *Compt. rend.*, 1882, 94, 1189

<sup>3</sup> Friedel, *Bull. Soc. chim.*, 1881 [n.s.] 41, 100

<sup>4</sup> Van der Plaats, *Compt. rend.*, 1855, 40, 52

<sup>5</sup> Stas, *Bull. Acad. Bruxelles*, 1849, 16, 1

<sup>6</sup> Scott, *Trans. Chem. Soc.*, 1897, 71, 577

<sup>7</sup> Lachg and Redtenbacher, *London*, 1841, 38, 137. In these and the succeeding calculations the following antecedent data have been assumed:  $O = 16.000$ ,  $Ag = 107.880$ ,  $H = 1.00762$ ,  $Na = 22.996$

<sup>8</sup> Marignac, *Oeuvres complètes*, 1846, 1, 184

## CARBÓN AND ITS ALLIES

spurting. Some results obtained by Maumené<sup>1</sup> were too low and will not be considered here. The general tendency is for all estimations involving ignition of silver salts to be a little too high, owing to slight volatilisation of silver.

Hardin,<sup>2</sup> in 1896, analysed silver acetate and benzoate by dissolving them in water, adding excess of potassium cyanide and electrolysing the solution. From his results the following values may be calculated:

$$\begin{array}{l} \text{C}_2\text{H}_3\text{O}_2\text{Ag} : \text{Ag} = 100 : 61.637, \text{ whence atomic weight of C} = 12.000 \\ \text{C}_7\text{H}_5\text{O}_2\text{Ag} : \text{Ag} = 100 : 17.125, \quad \quad \quad \text{C} = 12.001 \end{array}$$

In 1904 Parsons<sup>3</sup> analysed glucinum acetylacetonate and glucinum basic acetate, with the following results:

$$\begin{array}{l} (\text{C}_5\text{H}_7\text{O}_2)_2\text{Gl} : \text{GlO} = 100 : 12.1124 \\ (\text{C}_5\text{H}_7\text{O}_2)_6\text{O}(\text{Gl})_3 : 16\text{GlO} = 100 : 21.698 \end{array}$$

These equations give the values  $\text{Gl} = 9.112$  and  $\text{C} = 12.007$ .

Nevertheless, Scott,<sup>4</sup> in 1909, titrated carefully purified tetramethyl and tetra-ethyl-ammonium bromides with a solution of pure silver, and obtained the remarkably high values of  $\text{C} = 12.017$  and  $12.019$  respectively.

Later, however, he obtained the values  $\text{C} = 11.999$  and  $\text{C} = 12.002$  by experiments on the combustion of naphthalene and emmanic acid respectively. The description of these experiments is lacking.<sup>5</sup>

Richards and Hoover<sup>6</sup> have determined the value of the sodium carbonate-silver ratio to be

$$\text{Na}_2\text{CO}_3 : 2\text{Ag} = 29.13501 : 59.91676$$

from which it follows that if  $\text{Ag} = 107.88$ , the molecular weight of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is 105.995, whence the sum of the atomic weights  $2\text{Na} + \text{C} = 57.995$  ( $\text{O} = 16$ ).

From this the atomic weight of carbon may be determined if that of sodium is known. Assuming the latter to be 22.996,<sup>7</sup> the atomic weight of carbon is 12.003.

**Summary.** The mean value for the atomic weight of carbon arrived at by Scott in 1897, by summarising and correcting the results obtained by the combustion of carbon, was 12.0008. Worthy to be placed alongside this figure are Hardin's mean value, 12.0005, Parsons' value, 12.007, and Richards and Hoover's value, 12.003. Taking into account the values obtained by the physical method, it would appear that the atomic weight of carbon lies between 12.000 and 12.005, the value 12.003 being perhaps the best compromise. Guye in 1905<sup>8</sup>, and Brauner in 1908, advocated the value 12.002.<sup>8</sup>

The figure which appears in the International Table of Atomic Weights for 1917 is **C 12.005**.

<sup>1</sup> Maumené, *Ann. Chim. phys.*, 1846, [iii], 18, 41.

<sup>2</sup> Hardin, *J. Amer. Chem. Soc.*, 1896, 18, 990.

<sup>3</sup> Parsons, *J. Amer. Chem. Soc.*, 1904, 26, 721, 1905, 27, 1204.

<sup>4</sup> Scott, *Trans. Chem. Soc.*, 1909, 95, 1200. See also Thorpe, *Proc. Chem. Soc.*, 1909, 25, 285. Scott, *ibid.*, 1909, 25, 286.

<sup>5</sup> Scott, *Proc. Chem. Soc.*, 1909, 25, 310.

<sup>6</sup> Richards and Hoover, *J. Amer. Chem. Soc.*, 1915, 37, 95.

<sup>7</sup> See discussions in vol. ii of this series.

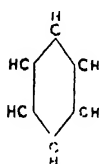
<sup>8</sup> Guye, *J. Chim. phys.*, 1905, 3, 321, 1906, 4, 174. Brauner, see Abegg and Auerbach, *Handbuch der anorganischen Chemie*, 1909, vol. iii, pt. ii, p. 28.

## COMPOUNDS OF CARBON

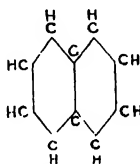
## COMPOUNDS OF CARBON WITH HYDROGEN

## THE HYDROCARBONS

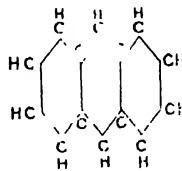
Carbon forms with hydrogen a large number and variety of compounds known as hydrocarbons. The existence of these many compounds depends on the union of carbon atoms with each other, which may result in the formation of open-chain or cyclic hydrocarbons. Examples of the latter are :



Benzene  
 $C_6H_6$



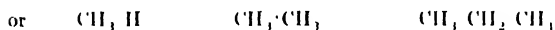
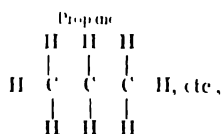
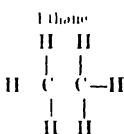
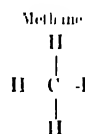
Naphthalene  
 $C_{10}H_8$



Anthracene  
 $C_{14}H_{10}$

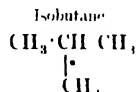
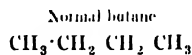
Most of the hydrocarbons find a place only in the study of "organic" chemistry, and it will be sufficient here to notice the main types of open-chain hydrocarbons, and describe in detail the properties of a few typical examples.

The simplest hydrocarbon is methane or marsh-gas,  $CH_4$ ; it is the first representative of a series of saturated, open-chain hydrocarbons, which may be represented thus:



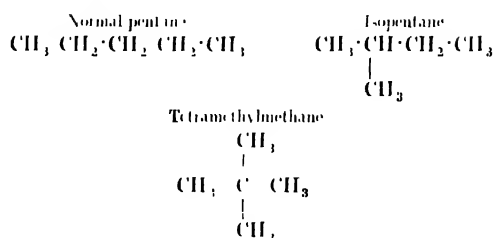
have the general formula  $C_nH_{2n+2}$ , and are known as the paraffin hydrocarbons.

When four or more carbon atoms are present in the molecule, branched chains may occur, with the phenomenon of isomerism. For example, there are two hydrocarbons of the formula  $C_4H_{10}$  :





and three of the formula  $C_5H_{12}$  :



The normal paraffins constitute an homologous series in which is shown a gradation in physical properties from member to member, thus :

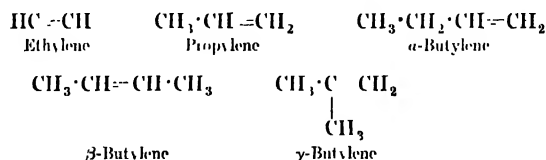
		B.P. (Atm. pressure)	Density
Normal pentane	$C_5H_{12}$	37° C.	0.627 at 14° C.
„ hexane	$C_6H_{14}$	69° C.	0.658 „ 20° C.
„ heptane	$C_7H_{16}$	98° C.	0.683 „ 20° C.
„ octane	$C_8H_{18}$	125° C.	0.702 „ 20° C.
„ nonane	$C_9H_{20}$	150° C.	0.718 „ 20° C.
„ decane	$C_{10}H_{22}$	173° C.	0.730 „ 20° C.

The boiling-points of the normal paraffins are higher than those of their isomers, e.g.

Normal butane	B.P.	-1° C.
Isobutane	„	-17° C.
Normal pentane	„	37° C.
Isopentane	„	31° C.
Tetramethylmethane	„	-10° C.

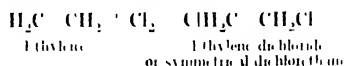
These differences may be attributed to the greater compactness of the branched as compared with the unbranched carbon chains.

Since methylene,  $CH_2$ , is unknown, the hydrocarbon ethylene,  $C_2H_4$ , is the first of the olefine series, whose general formula is  $C_nH_{2n}$ . These compounds contain two atoms of hydrogen fewer than the corresponding paraffin hydrocarbons. The two adjacent carbon atoms from each of which a hydrogen atom is lacking, are formulated as joined together by a double bond. In the case of olefine hydrocarbons containing four or more carbon atoms isomerism occurs owing to the double bond occupying different positions. The following are the constitutional formulae for the olefines  $C_2H_4$ ,  $C_3H_6$ , and  $C_4H_8$  :

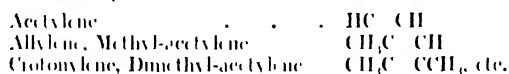


The olefine hydrocarbons are unsaturated, i.e. they form additive

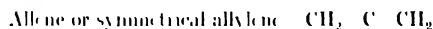
compounds which are paraffin hydrocarbons or their derivatives. In this process the double bond is ruptured, thus :



Acetylene,  $\text{C}_2\text{H}_2$ , is the first of a third series of hydrocarbons, named after the first member, and having the general formula  $\text{C}_n\text{H}_{2n-2}$ . These contain a triple bond and unite with four hydrogen atoms or their equivalent, forming paraffin hydrocarbons or their derivatives :



Isomeric with the acetylenes are the di-olufines, *e.g.*



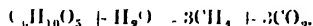
Oldine-acetylenes are known, *e.g.*  $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$ , and di-acetylenes, *e.g.*  $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$ .

## METHANE

Formula,  $\text{CH}_4$

**Occurrence.** - There are apparently three natural sources of methane (i) marshes, (ii) coal, (iii) petroleum springs.

(i) The gas-bubbles which are seen to rise through the water of stagnant pools consists of methane and nitrogen together with a little oxygen and carbon dioxide. The methane is produced by the bacterial fermentation of the cellulose of dead plants, and the chemical reaction has been represented as follows



(ii) Coal contains adsorbed methane ; and the presence of this gas in coal represents a later stage of the same kind of decomposition, which accounts for its formation in marshes (see under Coal, p. 59).

(iii) Inflammable gas, consisting chiefly of methane, escapes from holes in the earth in the neighbourhood of subterranean petroleum. Thus, at Baku, on the Caspian Sea, a "holy fire" has been burning for many centuries. Gas collected at Pittsburg, in the oil district of America, is conveyed fifteen miles in pipes and used as fuel ; that at Heathfield, Sussex, contains 94 per cent. of methane and 3 per cent. of ethane.<sup>1</sup>

Methane occurring near to petroleum must be considered the most volatile part of the petroleum so that the question of its origin there is the same as that of the petroleum itself.

**History.**—The escape of combustible gas from the earth is mentioned by Pliny, and the outbursts of flame in mines received the attention of Basil Valentine. Volta, in 1776, showed that a volume of methane required for its combustion four times the volume of oxygen that was required by an equal volume of hydrogen, and that it produced

<sup>1</sup> Dixon and Bone, *Proc. Chem. Soc.*, 1903, 19, 63

carbon dioxide when burnt. In 1785 Berthollet proved that the gas contained carbon and hydrogen; and in 1805 William Henry distinguished it from the denser ethylene.

Methane was thenceforth called *light carburetted hydrogen*, ethylene being heavy carburetted hydrogen. On account of its formation by the decay of vegetable matter in swamps, methane is likewise known as *marsh-gas*; and because it is the cause of explosions in coal-mines it is also called *fire-damp* (Ger. *Dampf* = vapour).

**Origin of Petroleum.**—Two theories have been proposed to account for the origin of petroleum: (i) that it owes its formation to the action of water on carbides; (ii) that it is formed by the decomposition of plant and animal remains.

(i) Berthelot<sup>1</sup> supposed that acetylides are formed by the action of carbon dioxide on the alkali metals at high temperature, from which acetylene is generated by the action of water; and Mendeléeff<sup>2</sup> assumed that subterranean iron carbides have similarly given rise to petroleum. Moissan<sup>3</sup> adopted Mendeléeff's view, which appears to be supported by the presence of methane in volcanic gases and liquid and solid hydrocarbons in lava,<sup>4</sup> and also by the discovery of occluded hydrocarbons in meteorites.<sup>5</sup>

It must be pointed out, however, that the theory of the production of hydrocarbons from inorganic materials postulates the high temperature necessary for the formation of metallic carbides, and that many geologists now discard the idea that the earth was once molten.

(ii) The formation of methane by the decomposition of vegetable matter and of various hydrocarbons in the destructive distillation of coal are facts that suggest that petroleum generally owes its origin to an organic source.

Engler distilled fish oil under pressure, and from the crude product obtained an illuminating oil, consisting of hydrocarbons and resembling kerosene.<sup>6</sup> Sadtler similarly obtained a mixture of hydrocarbons by distilling linseed oil.<sup>7</sup> Phillips proved the formation of methane in the slow decay of seaweed<sup>8</sup>; and Engler estimated from the annual catch of herring on the north coast of Germany that the total petroleum-supply of Galicia would be produced from fish in about 2500 years.<sup>9</sup> Other possible sources of petroleum are molluscs, radiates, and diatoms. The presence of optically active hydrocarbons in petroleum makes the organic source of this product practically certain,<sup>10</sup> and the occurrence of the oil in sedimentary rather than igneous rocks lends further support to the same view. There is little doubt, therefore, that petroleum owes its origin to an animal or vegetable rather than a mineral source.

**Synthesis of Methane.**—The synthesis of methane from its elements at high temperature was first announced by Bone and Jerdan<sup>11</sup> in 1897, but was questioned by Berthelot,<sup>12</sup> Pring and Hutton,<sup>13</sup> and Mayer and

<sup>1</sup> Berthelot, *Ann. Chim. Phys.*, 1866, [iv], 9, 481.

<sup>2</sup> Mendeléeff, *Ber.*, 1877, 10, 229. <sup>3</sup> Moissan, *Compt. rend.*, 1896, 122, 1462.

<sup>4</sup> O. Silvestri, *Gazzetta*, 1877, 7, 1; 1882, 12, 0.

<sup>5</sup> Wohler, *Annalen*, 1858, 109, 349. <sup>6</sup> Engler, *Ber.*, 1888, 21, 1816.

<sup>7</sup> Sadtler, *Proc. Amer. Phil. Soc.*, 1876, 36, 33.

<sup>8</sup> Phillips, *Amer. Chem. J.*, 1894, 16, 427. <sup>9</sup> Engler, *Ber.*, 1900, 33, 16.

<sup>10</sup> P. Walden, *Chem. Zeit.*, 1906, 30, 391, 1155, 1168.

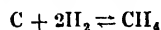
<sup>11</sup> Bone and Jerdan, *Trans. Chem. Soc.*, 1897, 71, 41.

<sup>12</sup> Berthelot, *Compt. rend.*, 1905, 40, 905; *Ann. Chim. Phys.*, 1905, [viii], 6, 183.

<sup>13</sup> Pring and Hutton, *Trans. Chem. Soc.*, 1906, 89, 1591.

Alt Mayer.<sup>1</sup> Bone and Coward,<sup>2</sup> however, reaffirmed the synthesis in 1908, and obtained 73 per cent. of the theoretical yield of methane by heating less than 0.1 gramm of highly purified sugar-charcoal to 1150° C. in a current of pure dry hydrogen. These conclusions were subsequently upheld by Pring<sup>3</sup>; and in 1910 Bone and Coward<sup>4</sup> obtained over 95 per cent. of the theoretical yield of methane by heating the sugar-charcoal in specially prepared porcelain tubes through which hydrogen was passed.

In the paper above referred to Mayer and Alt Mayer studied the equilibrium in the presence of a catalyst between carbon, hydrogen, and methane represented by the equation :



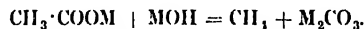
and expressed it as follows :

$$KT = -18,507 + 5.9934 T \log T + 0.002936 T^2 + RT \log \frac{P_{CH_4}}{P_{H_2}^2}$$

where T = abs. temp.,  $P_{H_2}$  and  $P_{CH_4}$  are the partial pressures of methane and hydrogen respectively, and K = 21.1. Their conclusion that methane cannot be formed from its elements at 1200° C. is not, however, in accordance with the facts established by Bone, Jordan, and Coward.

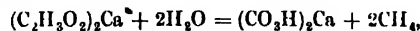
The synthesis of hydrocarbons at high temperatures and the "methane equilibrium" have been investigated by Pring and Fairlie,<sup>5</sup> who find that under special conditions at 1200° C. and under 10 to 60 c.m. pressure of hydrogen the ratio methane to ethylene produced is as 100 : 1, but that at 1400° C. it is as 10 : 1. When hydrogen is heated with carbon under a pressure of 30 to 50 atmospheres, equilibrium is reached in two hours at 1200°-1300° C., and in fifteen minutes above 1400° C. No saturated hydrocarbon but methane is formed between 1100° C. and 2100° C., and with a range of pressure up to 200 atmospheres; and the relative amount of methane produced increases with pressure according to the law of mass action as applied to the equation  $C + 2H_2 = CH_4$ . In accordance with these facts methane might be conveniently prepared by synthesis on a large scale by arranging suitable conditions.

**Preparation.**—(i) Methane is generally prepared for laboratory use by heating an acetate with caustic alkali, when the following reaction takes place :



It is usual to employ a mixture of anhydrous sodium acetate and soda-lime; to heat the mixture in a tube of hard glass or iron, or in a copper flask, and to collect the gas over water. Calcium acetate, also, may be heated with lime or baryta. The gas thus prepared may contain as much as 8 per cent. of hydrogen,<sup>6</sup> as well as ethylene.

(ii) Methane also results from the putrefactive hydrolysis of calcium acetate,<sup>7</sup> thus :



<sup>1</sup> Mayer and Alt Mayer, *Ber.*, 1907, 40, 2134.

<sup>2</sup> Bone and Coward, *Trans. Chem. Soc.*, 1908, 93, 1975.

<sup>3</sup> Pring, *Trans. Chem. Soc.*, 1910, 97, 498.

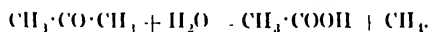
<sup>4</sup> Bone and Coward, *Trans. Chem. Soc.*, 1910, 97, 1218.

<sup>5</sup> Pring and Fairlie, *Trans. Chem. Soc.*, 1911, 99, 1796; 1912, 101, 91. See also Ipatieff, *J. prakt. Chem.*, 1913, [ii], 87, 479.

<sup>6</sup> Kolbe, *Ausfuhr. Lehrb. Org. Chem.*, 1854, i, 275.

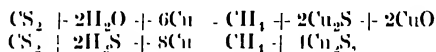
<sup>7</sup> Hoppe-Seyler, *Zeitsch. physiol. Chem.*, 1887, 11, 561.

and (iii) from the decomposition by sunlight of acetone in acetic acid solution :



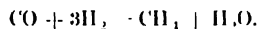
(iv) Methane may be prepared by the reduction of chloroform ( $\text{CHCl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ). This may be effected by passing their vapours together with excess of hydrogen through a red-hot tube, by heating the chlorine compound with copper, potassium iodide, and water in a tube,<sup>1</sup> or by reducing it with potassium amalgam in alcoholic solution.

(v) Methane is obtained by passing the vapour of carbon disulphide mixed with water-vapour or hydrogen sulphide over red-hot iron or copper :

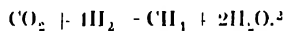


and by reducing carbon disulphide at  $120^\circ$  to  $110^\circ\text{C}$  with phosphonium iodide.

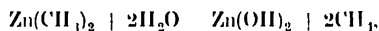
(vi) Carbon monoxide and hydrogen yield methane and water when submitted to the silent electric discharge :



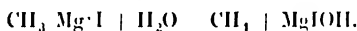
A similar action takes place at  $250^\circ\text{C}$  under the catalytic influence of reduced nickel, and at  $350^\circ\text{C}$  carbon dioxide is reduced in the same way :



(vii) Pure methane results from the action of water on zinc methyl, thus



as well as upon magnesium methyl iodide prepared by Grignard<sup>3</sup> :

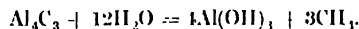


(viii) Methane is also obtained by the action of a metallic couple on methyl iodide in alcoholic solution. Gladstone and Tribe<sup>4</sup> employed a zinc-copper couple, but Bone and Wheeler<sup>5</sup> found that an aluminium-mercury couple is more efficient. The reaction is essentially



the methane, however, always contains a little hydrogen, which can be got rid of by passing the gas through a layer of oxidised palladium black at  $100^\circ\text{C}$ ., or by cooling to the temperature of liquid air, when methane condenses, but not hydrogen.

(ix) Still another method of obtaining methane is by the action of water on metallic carbides. Aluminium carbide, for example, reacts as follows<sup>6</sup> :



<sup>1</sup> Berthelot, *Ann. Chim. Phys.*, 1857, [iii], 51, 48; 1858, 53, 69.

<sup>2</sup> See Gantier, *Compt. rend.*, 1910, 150, 1564.

<sup>3</sup> Grignard, *Ann. Chim. Phys.*, 1901, 24, 438.

<sup>4</sup> Gladstone and Tribe, *Trans. Chem. Soc.*, 1884, 45, 154.

<sup>5</sup> Bone and Wheeler, *ibid.*, 1902, 81, 541.

<sup>6</sup> Moissan, *Compt. rend.*, 1894, 116, 16.

Campbell and Parker<sup>1</sup> have shown that methane prepared by this reaction contains a little hydrogen, which can be removed by mixing the gas with a slight excess of oxygen and passing the mixture over palladium-black. After removal of the remaining oxygen by alkaline pyrogallol solution, no impurity could be detected in the methane.

Other carbides, such as those of glucinum, thorium, and manganum, yield methane mixed with other hydrocarbons.

**Physical Properties.** Methane is a colourless gas without taste or smell, and is not poisonous. Its density at 0° C is 0.5576 (air = 1), whilst that corresponding to the molecular weight (16.03) would be 0.5539.<sup>2</sup> Consequently methane is slightly more compressible than an ideal gas, and its constants for van der Waals' equation are:  $a = 0.00376$ ,  $b = 0.001557$  (Olszewski), or  $a = 0.00357$ ,  $b = 0.001625$  (Dewar). The mean specific heat between 18° and 208° C is 0.5930,<sup>3</sup> and the ratio of the two specific heats is 1.313.<sup>4</sup> Its heat of combustion is, according to Thomson,<sup>5</sup> 211.900 calories, and according to Berthelot and Maignon,<sup>6</sup> 213.500 calories.

Methane is slightly soluble in water, but much more soluble in alcohol. Measurements of solubility have been made by Bunsen,<sup>7</sup> Henrich,<sup>8</sup> Winkler,<sup>9</sup> and Christoff.<sup>10</sup> The following equations are given by Henrich:

$$\begin{aligned}\text{For water, } \frac{V}{V'} &= 0.05473 - 0.0012265t + 0.000011959t^2 \\ \text{For alcohol, } \frac{V}{V'} &= 0.522745 - 0.00295882t + 0.0000177t^2\end{aligned}$$

Methane was first liquefied by Cailletet in 1877,<sup>11</sup> and its boiling-points at different pressures have been estimated by Wroblewski<sup>12</sup> and Olszewski.<sup>13</sup> The following figures are selected from those given by Olszewski:

Pressure	B.P. °C
10 atm	- 93.3
11 "	126.8
2.24 "	153.8
1.60 "	164.0
80 mm Hg	185.8
5 "	201.5

According, however, to Ladenburg and Kugel<sup>14</sup> methane boils at - 152.5° under 749 mm.

<sup>1</sup> Campbell and Parker, *Trans. Chem. Soc.*, 1913, 103, 1292. See also Hansen, *Anal. Phys. Quart.*, 1913, 11, 317.

<sup>2</sup> See also Baume and Petrol, *Compt. rend.*, 1909, 148, 39.

<sup>3</sup> Regnault, *Mém. d. P. Acad.*, 1862, 26, 1. <sup>4</sup> Cailletet, *Proc. Roy. Soc.*, 1893, 54, 101.

<sup>5</sup> Thomson, *Rep.*, 1891, 15, 3000. <sup>6</sup> Maignon, *Ann. Chem. Phys.*, 1893, [vi], 30, 555.

<sup>7</sup> Bunsen, *Gesammelte Methoden*, 2. Ausgabe, 1877, 214.

<sup>8</sup> Henrich, *Zeitsch. physikal. Chem.*, 1892, 9, 135.

<sup>9</sup> Winkler, *Rep.*, 1904, 34, 1117.

<sup>10</sup> Christoff, *Zeitsch. physikal. Chem.*, 1906, 55, 622.

<sup>11</sup> Cailletet, *Jahresber.*, 1877, 221.

<sup>12</sup> Wroblewski, *Compt. rend.*, 1881, 99, 136.

<sup>13</sup> Olszewski, *Compt. rend.*, 1885, 100, 940.

<sup>14</sup> Ladenburg and Kugel, *Rep.*, 1899, 32, 1820.

The critical temperature and pressure<sup>1</sup> are  $-81.8^{\circ}\text{C}$ . and 54.9 atm. (Olszewski), or  $-95.5^{\circ}\text{C}$ . and 50.0 atm. (Dewar). According to Cardoso,<sup>2</sup> however, the critical constants are: critical temperature,  $82.85^{\circ}\text{C}$ .; critical pressure, 45.60 atm.; critical density, 0.1623.

The density of liquid methane at  $-164^{\circ}\text{C}$ . is 0.415<sup>3</sup>; solid methane is snow-like and melts at  $-184^{\circ}\text{C}$ . The temperature and pressure at which solid, liquid, and gaseous methane co-exist (*i.e.* the triple point) have been found by Crommich<sup>4</sup> to be  $-183.15^{\circ}\text{C}$ . and 70 mm. of mercury. A previous determination by Olszewski gave  $-185.8^{\circ}\text{C}$ . and 80 mm.

On account of the large proportion of hydrogen in methane the flame of this hydrocarbon is but slightly luminous. Wright<sup>5</sup> found that the gas, when burnt in an Argand burner at the rate of 1 cubic foot per hour, gave a flame of 5.2 candle-power, whilst that of coal-gas examined at the same time was equal to 11.20 candle-power.

**Chemical Properties.** Methane is a saturated hydrocarbon, incapable of additive reactions. It undergoes metathesis, however, with chlorine, except when perfectly dry, yielding successively methyl chloride ( $\text{CH}_3\text{Cl}$ ), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ), and carbon tetrachloride ( $\text{CCl}_4$ ). Fluorine acts upon methane more, and bromine less vigorously, than chlorine, but iodine has no action upon this hydrocarbon.

Methane is very stable towards heat, but various and conflicting views have been held as to the manner of decomposition of this and other simple hydrocarbons.<sup>6</sup> It has been shown, however, by Bone and Coward<sup>7</sup> that methane is decomposed by heat into its elements without the production of ethylene, acetylene, etc.; that decomposition is inappreciable at  $700^{\circ}\text{C}$ . and that the rate of decomposition is about sixty times greater at  $985^{\circ}\text{C}$ . than at  $785^{\circ}\text{C}$ . Moreover the decomposition took place at the surface of the hot tube through which the gas was passed, and the carbon deposited was peculiarly hard and lustrous.

Methane is decomposed into its elements by electric sparks or by the electric arc. According to Berthelot,<sup>8</sup> however, acetylene and other hydrocarbons of high molecular weight are formed.

Methane burns in air or oxygen, forming water and carbon dioxide. According to Phillips<sup>9</sup> the lowest temperature at which the combustion of methane and oxygen can take place, that is when the mixed gases are passed over palladised asbestos, is  $401-414^{\circ}\text{C}$ .; but Denham<sup>10</sup> finds this temperature to lie between  $514^{\circ}\text{C}$ . and  $516^{\circ}\text{C}$ . The mechanism of the combustion of methane and other hydrocarbons has been studied by Bone and Wheeler.<sup>11</sup> These observers found that the slow reaction of methane with oxygen at temperatures between  $300^{\circ}\text{C}$ . and  $1000^{\circ}\text{C}$ . resulted in the simultaneous oxidation of carbon and hydrogen, thus:  $2\text{CH}_4 + 3\text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\text{O}$ , but that formaldehyde appeared as

<sup>1</sup> Dewar, *Phil. Mag.*, 1885, [v], 18, 210.

<sup>2</sup> Cardoso, *Arch. Sci. phys. nat.* 1913, [iv], 36, 97.

<sup>3</sup> Olszewski, *Wied. Annalen*, 1887, 31, 58.

<sup>4</sup> Crommich, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 666.

<sup>5</sup> Wright, *Trans. Chem. Soc.*, 1885, 47, 200.

<sup>6</sup> Bone and Coward, *ibid.*, 1908, 93, 1197.

<sup>7</sup> Bone and Coward, *loc. cit.*

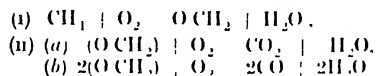
<sup>8</sup> Berthelot, *Compt. rend.*, 1898, 126, 567.

<sup>9</sup> Phillips, *Amer. Chem. J.*, 1894, 16, 163; see also *Zeitsch. anorg. Chem.*, 1891, 6, 219.

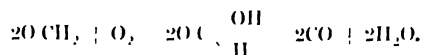
<sup>10</sup> Denham, *J. Soc. Chem. Ind.*, 1905, 24, 1202.

<sup>11</sup> Bone and Wheeler, *Trans. Chem. Soc.*, 1902, 81, 541, and 1903, 83, 1074.

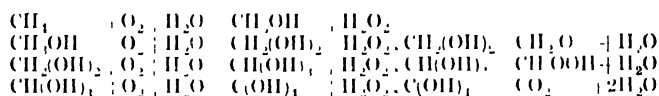
an intermediate and carbon dioxide as a final product. The following stages of oxidation are consequently recognised:



Reaction (ii b) may involve the intermediate production of formic acid, thus:

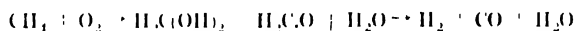


Armstrong<sup>1</sup> has put forward the view that the slow oxidation of a hydrocarbon such as methane is a series of hydroxylations in which water plays a part and hydrogen peroxide is produced; thus:



Thus gaseous oxidation becomes analogous to oxidation in the liquid state. Bone and Andrew<sup>2</sup> have shown, however, that the presence of water is not necessary to the combustion of a hydrocarbon, which may be supposed to be directly hydroxylated by oxygen.

When a mixture of methane and oxygen is exploded at constant volume and an initial pressure of from 10 to 50 atmospheres, the following is the course of the reaction:



The result of the explosion of the mixture ( $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$ ) shows that the affinity of methane for oxygen in explosions is from twenty to thirty times that of hydrogen.<sup>3</sup>

Methane forms an explosive mixture with air or oxygen. The intensity of the explosion increases from zero to a maximum, and diminishes again to zero within certain limits. The rates of propagation of the explosion have been studied by Mallard and Le Chatelier,<sup>4</sup> Emrich,<sup>5</sup> and Parker,<sup>6</sup> and Teclu<sup>7</sup> has found that the limits of explosibility of a mixture of methane and air are 3.20-3.67 and 7.16-7.88 per cent. of methane. Below the lower limit the mixture does not burn, above the higher limit it does not explode. Burrell and Robertson,<sup>8</sup> however, find that the lowest limit for the complete propagation of flame in a mixture of methane and air is between 3.75 and 4 per cent. of methane, and that the lowest ignition temperature for mixtures of methane and air is 590°C.

**Estimation of Methane.** Since there is no known absorbent for methane, this gas is estimated in a gaseous mixture by burning

<sup>1</sup> Armstrong, *Trans. Chem. Soc.*, 1903, 83, 1088.

<sup>2</sup> Bone and Andrew, *Trans. Chem. Soc.*, 1906, 89, 652.

<sup>3</sup> Bone, Davies, Gray, Hemstock, and Dawson, *Phil. Trans.*, 1910, [A], 215, 275.

<sup>4</sup> Le Chatelier, *Bull. Soc. chim.*, 1883, [ii], 39, 373.

<sup>5</sup> Emrich, *Monatsh.*, 1898, 19, 209.

<sup>6</sup> Parker, *Trans. Chem. Soc.*, 1915, 107, 328.

<sup>7</sup> Teclu, *J. prakt. Chem.*, 1907, [ii], 75, 212.

<sup>8</sup> Burrell and Robertson, *J. Ind. Eng. Chem.*, 1915, 7, 417.



it, and determining the amount of carbon dioxide produced either (a) volumetrically or (b) gravimetrically.

(a) To estimate the carbon dioxide volumetrically a given volume of gas is exploded with excess of air, and the volume after explosion noted. The residual gas is then shaken with caustic potash, and the diminution of volume thus brought about is that of the carbon dioxide, which is equal to the volume of methane originally present. If the methane was mixed with hydrogen the volume of the hydrogen is estimated by the following formula:

If  $a$  = contraction after explosion  
and  $y$  = contraction after exposure to potash = volume of methane,  
volume of hydrogen =  $\frac{1}{2}(a - 2y)$

According to Bone and Coward<sup>1</sup> small percentages of methane in presence of large excess of hydrogen cannot be accurately estimated by explosion. The hydrogen may, however, be previously removed and estimated by absorption in contact with palladium, and also by fractional combustion if the mixed gases containing excess of oxygen are passed over palladium sponge or palladium asbestos at 100° C., since at this temperature the hydrogen burns, but not the methane.<sup>2</sup>

(b) The carbon dioxide formed by the combustion of methane may be estimated gravimetrically after the manner of ultimate organic analysis by passing the methane through a tube containing red-hot copper oxide, and absorbing the resulting carbon dioxide in weighed potash bulbs after removing the water by calcium chloride.

## ETHYLENE

Formula,  $C_2H_4$

**History.** --Ethylene, Ethene, Olefiant gas, or Heavy Carburetted Hydrogen was first obtained by Becher from alcohol by heating it with sulphuric acid. It was mentioned by Priestley in his *Experiments and Observations on Air*, but first properly studied in 1795 by the four Dutch chemists, Deimann, Paets van Troostwyk, Bondt, and Lauwerenburgh, who observed the only liquid it produced on combination with chlorine. This liquid, ethylene dichloride, was named Dutch liquid from the nationality of its discoverers, and the gas itself was called olefiant (*i.e.* oil-forming) gas by Fourcroy.

The difference between ethylene and methane was observed by Henry in 1805, and the denser gas was called *heavy carburetted hydrogen* to distinguish it from methane, which was light carburetted hydrogen, these two gases being the only hydrocarbons known at that time.

The name ethylene is derived from the name of the alcohol (ethyl) whence it is prepared (*cf.* propylene from propyl alcohol); and the designation ethene is due to the Geneva Convention (1892), which applied the suffixes -ane, -ene, -ine in accordance with diminishing hydrogen content, thus:

$C_2H_6$	$C_2H_4$	$C_2H_2$
Ethane.	Ethene.	Ethine.

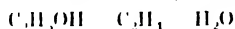
<sup>1</sup> Bone and Coward, *Trans. Chem. Soc.*, 1908, 93, 1979

<sup>2</sup> Hempel, *Gas Analysis*, Eng. edn., 1892, p. 135

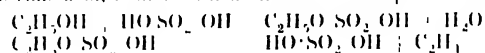
**Formation.** Ethylene is formed as a product of the dry distillation of many organic substances, e.g. salts of aliphatic acids, fats, resins, and coal.

**Synthesis.** Ethylene has been synthesised in small quantities from its elements. It has been found in small quantities, rarely exceeding 1 per cent, among the products of the interaction of hydrogen and various kinds of carbon at temperatures between 1800° C. and 2200° C.<sup>1</sup> When, however, the gaseous products are removed quickly from the neighbourhood of the heated carbon, and passed through a coil cooled in liquid air, the formation of ethylene is more marked. At 1200° C. and 10 to 60 cm. pressure the rate of formation of ethylene was one-hundredth that of the methane, but at higher temperatures the proportion of ethylene increased, till at 1400° C. the volume of the ethylene was one-tenth that of the methane.<sup>2</sup>

**Preparation.** (1) Ethylene is generally prepared by the dehydration of ethyl alcohol, the reaction being essentially



Zinc chloride, phosphoric anhydride, boric anhydride,<sup>3</sup> and concentrated sulphuric acid have been used as dehydrating agents. In the case of sulphuric acid the salt ester, known as ethyl sulphuric acid or sulphovinic acid, is first formed and then decomposes, thus



According to the method of Erdmeyer and Bunte<sup>4</sup> 25 grams of alcohol and 150 grammes of concentrated sulphuric acid are heated in a flask of 2-3 litres capacity to 160-170° C. and a mixture of 1 part of alcohol and 2 of sulphuric acid is dropped in. Ethylene is evolved, and is washed from alcohol and ether vapour with concentrated sulphuric acid, and from sulphur dioxide with caustic soda. Disadvantages of this process are charring and frothing, and the oxidation of some of the alcohol to carbon dioxide with the simultaneous evolution of sulphur dioxide from the sulphuric acid. Sand is sometimes added to prevent frothing, but, according to J. B. Senderens,<sup>5</sup> it acts also as a catalyst, causing the reaction to proceed at a lower temperature. Manganese sulphate, however, is a more effective catalyst. Newth<sup>6</sup> has shown that syrupy phosphoric acid may advantageously be substituted for sulphuric acid, and that a continuous stream of pure ethylene is obtained by dropping alcohol into 50 c.c. of the acid heated until its temperature attains 200-220° C. A further improvement consists in passing alcohol vapour through the heated phosphoric acid. This may be effected by dropping the alcohol slowly from a tap-funnel down a thistle-funnel closed with a cork. The alcohol then vaporises in the tube of the thistle-funnel within the generating flask, and blows through its finely drawn out point beneath the surface of the phosphoric acid. Or the alcohol may be boiled in a separate flask, and its vapour led into the phosphoric acid.<sup>7</sup>

<sup>1</sup> Pirng, *Trans. Chem. Soc.*, 1910, 97, 498.

<sup>2</sup> Pirng and Farber, *Trans. Chem. Soc.*, 1911, 99, 1796.

<sup>3</sup> Villard, *Ann. Chem. Phys.*, 1897, [vi], 10, 389.

<sup>4</sup> Bunte, *Annalen*, 1873, 168, 64; 1878, 192, 221.

<sup>5</sup> Senderens, *Compt. rend.*, 1910, 151, 392. see also Kreman, *Monatsh.*, 1910, 31, 211.

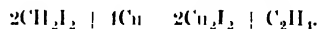
<sup>6</sup> Newth, *Trans. Chem. Soc.*, 1901, 79, 915.

<sup>7</sup> Prudeaux, *Chem. News*, 1916, 113, 277.

## CARBON AND ITS ALLIES

Other methods of obtaining ethylene are the following :

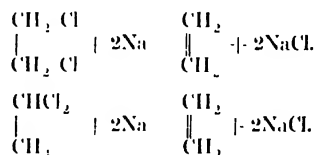
- (2) By heating methylene iodide with copper in a sealed tube :



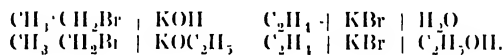
- (3) By the action of zinc upon ethylene bromide



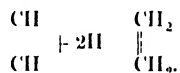
and of sodium on ethylene or ethyldene chloride :



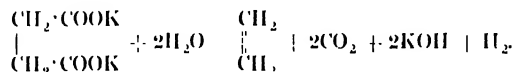
- (4) By the action of alcoholic potash or potassium ethoxide on ethyl bromide



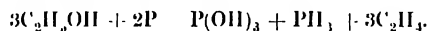
- (5) By the addition of hydrogen to acetylene through the action of zinc and ammonia on copper acetylide :



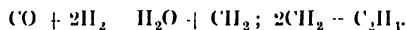
- (6) By the electrolysis of a concentrated solution of potassium succinate :



- (7) From alcohol and phosphorus,<sup>1</sup> thus :



- (8) From carbon monoxide and hydrogen by contact with nickel and palladium<sup>2</sup>



**Physical Properties of Ethylene.**—Ethylene is a colourless gas with an ethereal smell. It was first liquefied by Faraday in 1815 at  $-1^\circ\text{C}$ . under 42 atmospheres pressure. The vapour-pressure at various temperatures are thus given by Olszewski<sup>3</sup> and Villard<sup>4</sup> :

<sup>1</sup> Senderens, *Compt. rend.*, 1907, 144, 381, 1109.

<sup>2</sup> Orloff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1588.

<sup>3</sup> Olszewski, *Compt. rend.*, 1884, 99, 133.

<sup>4</sup> Villard, *Ann. Chim. Phys.*, 1897, [vi], 10, 389.

Olszewski		Villard	
Temp. °C	Vapour Pressure	Temp. °C	Vapour Pressure
-150	9.8 mm	101	1.0 atm
132	56 "	60	7.5 "
111	316 "	0	10.2 "
-103	750 "	+ 9.9	50.1 "

Thus the boiling-point of ethylene at atmospheric pressure is about 101 °C. Cardoso and Ann<sup>1</sup> give B.P. = 101.3 °C.

The vapour pressures<sup>2</sup> of ethylene at temperatures below its normal boiling-point may be calculated from the equation

$$\log P = \frac{767.8}{t} + 7.133.$$

The following critical data for ethylene have been determined by different observers

	Critical Temperature	Critical Pressure
Van der Waals <sup>3</sup>	9.2° C.	58.0 atm.
Dewar <sup>4</sup>	10.1 °C.	51.0 "
Olszewski <sup>5</sup>	10.0 °C.	51.7 "
Cardoso and Ann <sup>1</sup>	9.50 - 10° C.	50.65 - 10 atm.

The constants  $a$  and  $b$  in van der Waals' equation are for ethylene 0.00889 and 0.00251 (Dewar<sup>4</sup>) or 0.00877 and 0.00251 (Olszewski<sup>5</sup>) respectively.

The density of gaseous ethylene is 0.9852 (air = 1), whilst the density of a perfect gas of molecular weight 28.03 would be 0.9681.

Liquid ethylene solidifies at -169 °C.<sup>6,7</sup> the density<sup>7</sup> of the liquid at its boiling-point is 0.6095, and at the melting point 0.6585. According to Cailliet and Mathias,<sup>8</sup> however, liquid ethylene has a density of 0.306 at 6.1 °C. The cryoscopic constant<sup>9</sup> of dry ethylene is 125, that of the moist compound 118. The specific heat of ethylene between 10 °C and 220 °C is 0.1010<sup>10</sup>, its heat of combustion is 341,100 calories (Berthelot and Matignon<sup>11</sup>) or 333,300 calories (Thomsen<sup>12</sup>).

Ethylene is slightly soluble in water, but much more soluble in alcohol. Henrich<sup>13</sup> expresses its solubility in these two solvents by the following equations.

<sup>1</sup> Cardoso and Ann *J. Chem. phys.*, 1912, 10, 401.

<sup>2</sup> Burrell and Robertson *J. Amer. Chem. Soc.*, 1915, 37, 1893.

<sup>3</sup> Van der Waals *Beiblätter*, 1880, 4, 704.

<sup>4</sup> Dewar, *Phil. Mag.*, 1884, [vi], 18, 210.

<sup>5</sup> Olszewski, *Phil. Mag.*, 1895, 39, 188.

<sup>6</sup> Olszewski, *Monatsh.*, 1887, 8, 69.

<sup>7</sup> Ladenburg and Krügel, *Ber.*, 1899, 32, 1820.

<sup>8</sup> Cailliet and Mathias, *Compt. rend.*, 1882, 94, 1563, 1886, 102, 1202.

<sup>9</sup> Moles, *Anal. Fis. Quim.*, 1912, 10, 131.

<sup>10</sup> Regnault, *Mém. d'Ét. nat.*, 1862, 26, 1.

<sup>11</sup> Berthelot and Matignon, *Ann. Chem. Phys.*, 1893, [vi], 30, 555.

<sup>12</sup> Thomsen, *Thermochemische Untersuchungen*, 1882, ii, 97.

<sup>13</sup> Henrich, *Zeitsch. physikal. Chem.*, 1892, 9, 175.

Solubility of ethylene in water at  $t^{\circ}\text{C}.$ :

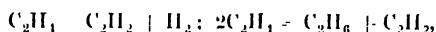
$$c = 0.25487 - 0.0088312t + 0.00017417t^2.$$

Solubility of ethylene in alcohol at  $t^{\circ}\text{C}.$ :

$$c = 3.5876 - 0.056153t + 0.00062369t^2.$$

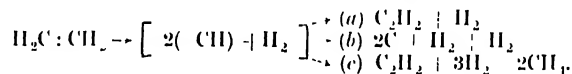
Ethylene under pressure forms with water the hydrate  $\text{C}_2\text{H}_4.6\text{H}_2\text{O}$ .<sup>1</sup>

**Chemical Properties of Ethylene.** *Decomposition.*—It was shown by Dalton and Henry<sup>2</sup> that carbon and hydrogen result from passing electric sparks through the gas. Marchand<sup>3</sup> believed that ethylene was decomposed into carbon and methane ( $\text{C}_2\text{H}_4 = \text{C} + \text{CH}_4$ ) at a bright red heat, and Buff and Hofmann<sup>4</sup> observed this result when a platinum wire was heated electrically to dull redness in the gas. No account, however, was taken by these observers of intermediate products which are undoubtedly formed. Berthelot<sup>5</sup> represented the thermal decomposition of ethylene thus:



acetylene being the ultimate decomposition product, whether  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , or  $\text{C}_2\text{H}_4$  is decomposed, which subsequently polymerises to benzene, etc. Lewes<sup>6</sup> represented the decomposition thus:  $3\text{C}_2\text{H}_4 = 2\text{C}_2\text{H}_2 + 2\text{CH}_4$ ; but the views of Bone and Coward<sup>7</sup> differ somewhat from any of the foregoing.

According to these observers the primary effect of high temperature upon ethylene is to eliminate hydrogen and simultaneously loosen the "double bond" between the carbon atoms, so that the residues  $\cdot\text{CH}_2$  and  $\cdot\text{CH}$  have a momentary existence. These residues may then either (a) form ethylene or acetylene, (b) break down into carbon and hydrogen, or (c) be hydrogenised to methane, thus:



Bone and Coward observed the generation of brown vapours which condensed to a viscous tar when ethylene at a pressure of 365 mm. circulated through a tube at  $570-580^{\circ}\text{C}$ . These products were complex, but consisted of aromatic hydrocarbons formed by the polymerisation of acetylene or  $\cdot\text{CH}$  residues.

**Polymerisation.**—Ethylene polymerises at high temperature and pressure in presence of catalysts. The product is a complex mixture containing pentane, isopentane, hexane, ethylene hydrocarbons, and naphthenes.<sup>8</sup>

**Additive Reactions.**—As an unsaturated hydrocarbon ethylene is capable of numerous additive reactions. It combines with hydrogen to form ethane ( $\text{C}_2\text{H}_6$ ) under the catalytic influence of platinum-black

<sup>1</sup> Villard, *Ann. Chim. Phys.*, 1897, [vi], 11, 289.

<sup>2</sup> Dalton, *New System*, pt. i, 1808, i, pp. 440, 447; *Phil. Trans.*, 1809, 99, 446.

<sup>3</sup> Marchand, *J. prakt. Chem.*, 1839, 36, 378.

<sup>4</sup> Buff and Hofmann, *Annalen*, 1860, 113, 129.

<sup>5</sup> Berthelot, series of papers in *Ann. Chim. Phys.*, 1863-1869.

<sup>6</sup> Lewes, *Proc. Roy. Soc.*, 1891, 55, 90; 1895, 57, 394.

<sup>7</sup> Bone and Coward, *Trans. Chem. Soc.*, 1908, 93, 1201.

<sup>8</sup> Ipatieff and Rutala, *Ber.*, 1913, 46, 1748.

at atmospheric temperature<sup>1</sup>; and finely divided nickel produces an almost quantitative yield of ethane at 130°–150° C.<sup>2</sup> Ethylene unites directly with chlorine, bromine, and iodine to form the corresponding dihalides ( $C_2H_4X_2$ ), and also with  $NO_2$ ,  $S_2Cl_2$ , and  $SO_2$ . It combines with  $HBr$  and  $HI$  at 100° C., but not with  $HCl$ , forming  $C_2H_5Br$  and  $C_2H_5I$  respectively. It unites with concentrated sulphuric acid, slowly at atmospheric temperature, quickly at 160°–171° C., forming ethyl-sulphuric or sulphuric acid,  $C_2H_5HSO_4$ , with fuming sulphuric acid it

forms ethionic acid,  $\begin{array}{c} CH_2 \cdot OSO_3H \\ | \\ CH_2 \cdot SO_3H \end{array}$  or its anhydride, ethylsulphate,

$\begin{array}{c} CH_2 \cdot O \cdot SO_2 \\ | \\ CH_2 \cdot OSO_2 \end{array}$ . Fuming sulphuric acid is used for the absorption of ethylene in gas analysis.

Chlorosulphuric acid ( $Cl \cdot SO_3H$ ) produces isethionyl chloride,  $\begin{array}{c} CH_2 \cdot Cl \\ | \\ CH_2 \cdot SO_3H \end{array}$ , which yields isethionic acid  $\left( \begin{array}{c} CH_2OH \\ | \\ CH_2 \cdot SO_3H \end{array} \right)$  with water.

Hypochlorous acid forms glycol monochlorohydrin,  $\begin{array}{c} CH_2 \cdot Cl \\ | \\ CH_2OH \end{array}$ , and fuming nitric acid yields ethylene nitrate  $C_2H_4(N_2O_5)$ . Although water does not combine directly with ethylene to produce ethyl alcohol, the latter may be obtained by hydrolysing the additive compound with sulphuric or nitric acid.

There is evidence of the existence of an oxonium compound<sup>3</sup> with methyl ether  $\begin{array}{c} CH_3 \\ | \\ CH_3 \cdot O \cdot CH_2 \\ | \\ CH_3 \end{array}$ .

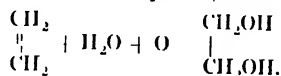
Ethylene forms the following double compounds with salts:  $C_2H_4 \cdot FeBr_2$ ,  $C_2H_4 \cdot PtBr_2$ ,  $C_2H_4 \cdot 2KCl$ , and the following compounds with mercuric salts<sup>4</sup>:

- (1) Ethene mercuric salts,  $CH_2 \cdot CH \cdot HgX$
- (2) Ethanol mercuric salts,  $H(O \cdot CH_2 \cdot CH \cdot HgX)$
- (3) Ethyl ether mercuric salts,  $O(CH_2 \cdot CH_2 \cdot HgX)_2$
- (4) Polymerised ethene mercuric salts  $(CH_2 \cdot CH \cdot HgX)_n$ .

It is supposed that the saturated compound  $NCH_2 \cdot CH_2 \cdot HgX$  is first formed and then that it loses  $HX$  (1) or undergoes hydrolysis (2), which may be followed by condensation (3).

Ethylene also forms an unstable compound<sup>5</sup> with cuprous chloride:  $C_2H_4 \cdot CuCl$ .

**Oxidation.** Through the careful oxidation of ethylene by cold dilute permanganate solution ethylene glycol is produced:



<sup>1</sup> De Wilde, *Ber.*, 1871, 7, 374

<sup>2</sup> Sabatier and Sendraus, *Compt. rend.*, 1897, 124, 616, 1378, 1901, 1900, 131, 267.

<sup>3</sup> Baume and Germann, *Compt. rend.*, 1911, 153, 569

<sup>4</sup> Hofmann and Sand, *Ber.*, 1900, 33, 1310

<sup>5</sup> Manchot and Braudt, *Annalen*, 1909, 370, 286

More vigorous oxidation by permanganic, chromic, or nitric acid produces formic, acetic, and oxalic acids, and carbon dioxide.

*Combustion of Ethylene and of Hydrocarbons in general.* Ethylene burns with a flame of considerable luminosity. This is equal, according to Frankland,<sup>1</sup> to 68.5 candles when the gas is burnt at the rate of 5 cubic feet per hour, that of methane being equal to only about 5 candles. Ethylene is the chief cause of the luminosity of coal-gas, in which it is present to the extent of 2.5 per cent.

There are three possible views of the manner of combustion of a hydrocarbon: (i) the preferential combustion of hydrogen with the consequent separation of carbon; (ii) the preferential combustion of carbon with formation of  $(CO + H_2)$ ; (iii) the combustion of the hydrocarbon as a whole without previous dissociation or preferential combustion.

The first view, although it survived till 1892, has been discredited. To disprove it, it is sufficient to show that the outer zone of a hydrocarbon flame contains burning hydrogen, and that the innermost part of a Bunsen flame consists chiefly of hydrogen and carbon monoxide.

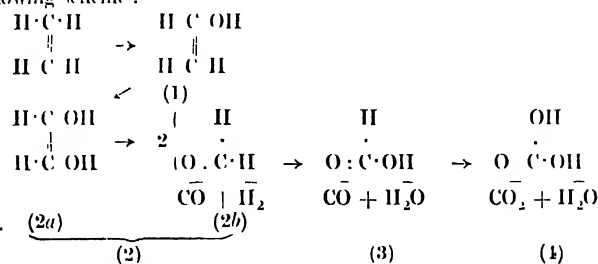
The second view was held by Dalton,<sup>2</sup> was put forward again by Kersten in 1861,<sup>3</sup> was reinforced by Smithells and Ingle in 1892,<sup>4</sup> and was revived by Misch<sup>5</sup> in 1905.

The third view, which is the outcome of the researches of Bone and his co-workers, and to which reference is made under methane, may now be noticed.

Much of this work has been concerned with the slow combustion of hydrocarbons below their temperatures of ignition, but in a paper on the "Explosive Combustion of Hydrocarbons" Bone and Drugman<sup>6</sup> contend that the initial changes are the same whether they take place below or above the temperature of ignition of the gas.

Bone and Wheeler<sup>7</sup> conclude that the combustion of a hydrocarbon is a process of hydroxylation, and that "oxygen initially enters the hydrocarbon and is distributed between the carbon and hydrogen, giving rise to unstable hydroxylated molecules which, sooner or later, according to the rapidity of the process, undergo thermal decompositions into simpler products."

The combustion of ethylene is accordingly represented by the following scheme.



<sup>1</sup> Frankland, *Trans. Chem. Soc.*, 1885, 47, 238.

<sup>2</sup> Dalton, *New System*, 1808, vol. i, 137, 144.

<sup>3</sup> Kersten, *J. prakt. Chem.*, 1861, 84, 310.

<sup>4</sup> Smithells and Ingle, *Trans. Chem. Soc.*, 1892, 61, 204.

<sup>5</sup> Misch, *J. Gasbeleuchtung*, 1905, 48, 802.

<sup>6</sup> Bone and Drugman, *Trans. Chem. Soc.*, 1906, 80, 678.

<sup>7</sup> Bone and Wheeler, *Trans. Chem. Soc.*, 1901, 85, 1637.

So the stages are : (1) vinyl alcohol, (2) formaldehyde, (3) formic acid, (4) carbonic acid—the three latter substances yielding as secondary products carbon monoxide, hydrogen, carbon dioxide, and water. Formaldehyde is regarded as the most prominent intermediate oxidation product.

No separation of carbon, such as takes place in ordinary hydrocarbon flames, is provided for in the above scheme. This separation takes place only when the supply of oxygen is insufficient to burn the ethylene to formaldehyde; then there result from thermal decomposition carbon, hydrogen, methane, and traces of acetylene. Thus the luminosity of a flame is still to be accounted for by the liberation of carbon consequent upon the thermal decomposition of its hydrocarbon gases; but side by side with this decomposition the reactions established by Bone and his co-workers take place.

**Estimation of Ethylene.** The amount of ethylene in a gaseous mixture is easily estimated by taking advantage of one of the additive reactions of which this gas is capable. Since fuming sulphuric acid so readily absorbs this gas, the latter is estimated by the loss of volume the gaseous mixture undergoes in contact with the acid.

### ACETYLENE

Formula,  $C_2H_2$

Acetylene or Ethine was discovered by Edmund Davy<sup>1</sup> in 1836, but was first investigated by Berthelot,<sup>2</sup> to whom the name Acetylene is due. Berthelot<sup>3</sup> produced this gas synthetically by striking the electric arc between carbon poles in an atmosphere of hydrogen :



Bone and Jordan<sup>4</sup> have investigated this action and find that methane and ethane are also produced, so that when equilibrium is attained the issuing gas has the following approximate composition :

Hydrogen	.	.	.	.	90-91 per cent.
Acetylene	.	.	.	.	7-8 "
Methane	.	.	.	.	1-25 "
Ethane	.	.	.	.	0-75 "

They are of opinion that these hydrocarbons are produced synthetically and independently, so that the acetylene does not result from the thermal decomposition of the other hydrocarbons.

It was further shown by Berthelot<sup>5</sup> that acetylene is produced when ethylene or the vapour of alcohol is passed through a red-hot tube, and also by the action of electric sparks on methane, ethylene, or a mixture of cyanogen and hydrogen. The formation of acetylene from ethylene by the action of heat has been confirmed by Bone and Coward,<sup>6</sup> but the same observers have shown that methane does not produce acetylene by thermal decomposition.

<sup>1</sup> Davy, *B. A. Reports*, 1836, p. 62.

<sup>2</sup> Berthelot, *Ann. Chim. Phys.*, 1859, [iii], 57, 82.

<sup>3</sup> Berthelot, *Ann. Chim. Phys.*, 1868, [iv], 13, 143.

<sup>4</sup> Bone and Jordan, *Trans. Chem. Soc.*, 1901, 79, 1012.

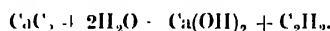
<sup>5</sup> Berthelot, *Ann. Chim. Phys.*, 1863 [iii], 67, 52, 1866, [iv], 9, 413, 1868, [v], 13, 143.

<sup>6</sup> Bone and Coward, *Trans. Chem. Soc.*, 1908, 93, 1201.



**Preparation.**—Acetylene is formed when a Bunsen burner “strikes back” and burns at the base. At the same time a peculiar and penetrating odour is smelt which, although not due to acetylene itself, serves to draw attention to the improper burning of the coal-gas. It is usual to attribute this production of acetylene to the imperfect combustion of the hydrocarbons present in the coal-gas, but it is probable that this gas is produced by the thermal dissociation of ethylene, and then escapes into the air owing to imperfect combustion.

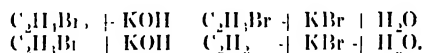
It was first observed by Wohler in 1862<sup>1</sup> that acetylene is formed by the action of water on calcium carbide:



The carbide was prepared on a large scale by Willson in 1892, and independently by Moissan<sup>2</sup> slightly later, by heating together lime and charcoal in the electric furnace. “Carbide” is now an important article of commerce owing to the employment of acetylene as an illuminant. It is prepared by heating limestone with coke or small coal in an electric furnace, and contains as impurities calcium sulphide, phosphide and silicide, and magnesium nitride, as well as the silicides of carbon and iron and also graphite. The acetylene generated from this carbide consequently contains hydrogen sulphide, phosphine, ammonia, and other impurities; and these are got rid of by absorption in water and oxidation by bleaching powder and other reagents.

Acetylene is formed by removing HBr from ethylene dibromide by boiling it with alcohol potash,<sup>3</sup> just as ethylene is obtained from ethyl bromide.

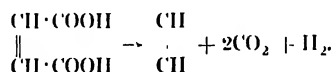
HBr is removed from the dibromide in two stages, thus:



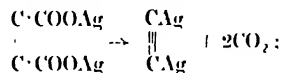
Sodium abstracts chlorine from chloroform yielding acetylene:



Electrolysis of solutions of the alkali salts of malic and fumaric acids produces acetylene, just as electrolysis of alkali succinate yields ethylene:



The silver salt of acetylene dicarboxylic acid is decomposed by hot water, yielding silver acetylide and carbon dioxide:



and from silver acetylide pure acetylene is obtained by the action of acid.

**Physical Properties.**—Pure acetylene is a colourless gas with an ethereal smell. It is liquefied more easily than ethylene or methane,

<sup>1</sup> Wohler, *Annalen*, 1862, 124, 267.

<sup>2</sup> Moissan, *Compt. rend.*, 1892, 115, 1031.

<sup>3</sup> Sawitsch, *Jahresber.*, 1861, p. 616.

and was first obtained in the liquid state by Caillctet<sup>1</sup> in 1877. The vapour-pressures of solid and liquid acetylene at various temperatures have been determined by Ausdell,<sup>2</sup> Villard,<sup>3</sup> Kuenen,<sup>4</sup> and McIntosh.<sup>5</sup> Some of the values determined by Villard, with which those of Kuenen and McIntosh are in close agreement, are:

Temp. °C.	Vapour Pressure	Temp. °C.	Vapour Pressure
- 90	0.69 atm. (solid)	- 10	7.7 atm.
- 85	1.00 (solid)	0	26.05 .
- 81	1.25 (M.P.)	11.5	31.8 .
- 70	2.22 „ (liquid)	20.2	12.8 „

It is noteworthy that at the melting-point of solid acetylene ( - 81°) the vapour-pressure is equal to 1.25 atmosphere, and that at - 85° solid acetylene vapourises at atmospheric pressure. That is to say, solid acetylene, like solid arsenic for instance, sublimates when heated under atmospheric pressure, and can only be melted under greater pressure. When liquid acetylene evaporates in the air it solidifies to a snowlike mass.

According to Ladenburg and Krugel<sup>6</sup> the sublimation temperature of acetylene is - 82.4° C., and according to McIntosh<sup>7</sup> - 83.6° C. at 760 mm. pressure. This latter observer found - 81.5° C. at 895 mm. to be the triple point at which solid, liquid, and gaseous acetylene can co-exist in equilibrium.

The critical data according to Villard (1), Kuenen (2), and McIntosh (3) are:

	(1)	(2)	(3)
Critical pressure in atm.	61.1	61.0	61.6
„ temperature ° C.	35.0	35.25	36.5
„ volume	—	—	83 c.c.

According to Mathias<sup>8</sup> the critical temperature is 37.05° C. and the critical density 0.2316, but Cardoso and Baume find critical temperature 35.5° C. and critical pressure 61.5 atm.<sup>9</sup>

The constants for van der Waals' equation are<sup>7</sup>:  $a = 0.0880$ ;  $b = 0.00230$ .

The density of acetylene under normal conditions is 0.92 (air = 1), the theoretical value being 0.988, the ratio of the specific heats<sup>10</sup>;  $\frac{C_p}{C_v} = 1.26$ ; the molecular heat of vapourisation for liquid acetylene at - 81.2° C. = 5080 calories, for solid acetylene at - 83.6° C. = 5490 calories.

<sup>1</sup> Caillctet, *Compt. rend.*, 1877, 85, 851.

<sup>2</sup> Ausdell, *Proc. Roy. Soc.*, 1879, 29, 209.

<sup>3</sup> Villard, *Compt. rend.*, 1895, 120, 1262.

<sup>4</sup> Kuenen, *Zeitsch. physikal. Chem.*, 1897, 24, 667.

<sup>5</sup> McIntosh, *J. Physical Chem.*, 1907, 11, 307.

<sup>6</sup> Ladenburg and Krugel, *Ber.*, 1900, 33, 638.

<sup>7</sup> McIntosh, *J. Physical Chem.*, 1907, 11, 307.

<sup>8</sup> Mathias, *Compt. rend.*, 1909, 148, 1102.

<sup>9</sup> Cardoso and Baume, *Compt. rend.*, 1910, 151, 141.

<sup>10</sup> Maneuvrier and Fournier, *Compt. rend.*, 1897, 124, 183.

The density of liquid acetylene at  $-80^{\circ}\text{C}$ . is 0.613, and of the solid at the same temperature 0.72.<sup>1</sup> Thus the molecular volume of liquid acetylene is 12, and this value supports the acetylidene formula  $\text{C}:\text{CH}_2$  of Nef.

On the other hand, Mathews<sup>2</sup> has shown physical reasons for rejecting the acetylidene formula in favour of the more usual and symmetric formula  $\text{CH}\equiv\text{CH}$ .

The heat of combustion of acetylene, according to Thomsen,<sup>3</sup> is 310,050 calories; and this value subtracted from the sum of the heats of formation of water and carbon dioxide (262,280) gives  $-17,770$  calories, as the heat of formation of acetylene.

Berthelot and Matignon<sup>4</sup> obtained the values 315,700 and  $-58,000$  calories and Mixer<sup>5</sup> 313,800 and  $-51,100$  calories, respectively.

*Solubility of Acetylene.* Acetylene is more soluble in water and other solvents than ethylene, and much more soluble than methane. One volume of water dissolves about 1.1 vol. of acetylene at atmospheric temperature, and the following coefficients are given by Winkler<sup>6</sup>:

$0^{\circ}\text{C}$	1.73
$10^{\circ}\text{C}$	1.31
$20^{\circ}\text{C}$	1.03
$30^{\circ}\text{C}$	0.84

At low temperature acetylene forms with water the crystalline hydrate  $\text{C}_2\text{H}_2 \cdot 6\text{H}_2\text{O}$ ,<sup>7</sup> whose dissociation pressure is as follows:

Temperature, $^{\circ}\text{C}$	0	7	15
Dissociation pressure	5.75	12	33 atm

Acetylene is much more soluble in organic solvents such as methyl and ethyl alcohol, ethyl acetate and acetone, than it is in water. Alcohol dissolves about six times its volume of acetylene, and acetone twenty-five times its volume at  $15^{\circ}\text{C}$ . and atmospheric pressure, and 300 times its volume under a pressure of 12 atmospheres.<sup>8</sup> These facts are made use of for the storage of acetylene as an illuminant. At  $-80^{\circ}\text{C}$ . acetone dissolves 2000-2500 its volume of acetylene, and thereby expands to four or five times its original volume.<sup>9</sup>

A solution of acetylene in benzene shows a normal molecular weight cryoscopically.<sup>10</sup> Acetylene forms crystalline compounds with alcohol, ether, and acetone.<sup>11</sup> Palladium-black and colloidal palladium adsorb acetylene.<sup>12</sup>

**Chemical Properties.**—In common with many endothermic compounds acetylene is liable to explosive decomposition. The explosibility

<sup>1</sup> McIntosh, *J. Physical Chem.*, 1907, **11**, 306.

<sup>2</sup> Mathews, *J. Physical Chem.*, 1913, **17**, 183, 320.

<sup>3</sup> Thomsen, *Thermochemische Untersuchungen* (Dr. J. Traube), Enke, (Stuttgart), 1906, p. 293.

<sup>4</sup> Berthelot and Matignon, *Ann. Chim. Phys.*, 1893, [vi], 30, 555.

<sup>5</sup> Mixer, *Am. J. Sci. (Sill.)*, 1901, [iv], 12, 317.

<sup>6</sup> Winkler, *Zeitsch. physikal. Chem.*, 1906, 55, 352.

<sup>7</sup> Villard, *Compt. rend.*, 1895, **120**, 1262.

<sup>8</sup> Claude and Hess, *Compt. rend.*, 1897, **124**, 626.

<sup>9</sup> Claude, *Compt. rend.*, 1899, **128**, 303; d'Arsonval, *Compt. rend.*, 1901, **133**, 980; see also James, *J. Ind. Eng. Chem.*, 1913, 5, 115.

<sup>10</sup> Garrell and Fawcett, *Att. R. Acad. Lancet*, 1904, [v], 13, 1, 115.

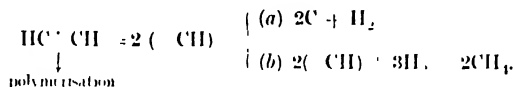
<sup>11</sup> McIntosh, *J. Physical Chem.*, 1907, **11**, 307.

<sup>12</sup> Paal and Hohenegger, *Ber.*, 1910, **43**, 2684, 2692; 1913, 46, 128.

of this gas has been studied by Berthelot<sup>1</sup> in conjunction with Vieille<sup>2</sup> and Le Châtelier.<sup>3</sup> Under ordinary atmospheric pressure acetylene is not exploded by a red-hot wire, or by mercury fulminate, but towards two atmospheres it becomes explosive, and carbon separates from it in the form of fine soot. It is consequently forbidden in this and some other countries to store acetylene under a pressure of more than 100 inches of water over atmospheric pressure; it may, however, be safely compressed in contact with acetone.

**Decomposition.** At ordinary temperature acetylene undergoes very slow spontaneous decomposition. Rapid decomposition sets in at 780°C.,<sup>4</sup> and in the presence of copper powder, as a catalyst, at 100–500°C. The thermal decomposition of acetylene has been studied by Bone and Coward,<sup>5</sup> who find that the primary effect of heat upon this gas may be one of polymerisation or dissolution according to temperature. Polymerisation produces tarry matter containing benzene, etc.; dissolution separates the residues (C<sub>2</sub>H<sub>2</sub>) which may split into their elements or become hydrogenised, yielding methane. At the same time ethylene and ethane may be formed at low temperatures by the union of liberated hydrogen with acetylene.

The following scheme represents the thermal decomposition of acetylene:



The tendency of acetylene to polymerise reaches a maximum between 600 and 700°C., and rapidly diminishes towards 1000°C., above which temperature the gaseous product consists of hydrogen with a little methane. The products of polymerisation are very complex. Meyer and Tanzen<sup>6</sup> have identified no fewer than seventeen coal-tar constituents amongst the pyrogenetic condensation-products of acetylene.

Sunlight, the silent electric discharge, platinum-black, and finely divided iron, nickel, and cobalt promote polymerisation, which may take place even at atmospheric temperature.

According to Tschitschibabin<sup>7</sup> acetylene undergoes three principal kinds of reaction in presence of different catalysts:

- (i) Local decomposition into carbon and hydrogen, accompanied by polymerisation to aromatic hydrocarbons.
- (ii) Condensation to solid hydrocarbons.
- (iii) Hydrogenation of acetylene and aromatic hydrocarbons, with the formation of hydrocarbons of the paraffin, olefine, and cyclic series.

When acetylene and ammonia are passed over alumina, ferric oxide,

<sup>1</sup> Berthelot, *Compt. rend.*, 1881, 93, 616.

<sup>2</sup> Vieille, *Compt. rend.*, 1897, 124, 1000; 1899, 128, 777.

<sup>3</sup> Le Châtelier, *Compt. rend.*, 1899, 129, 127.

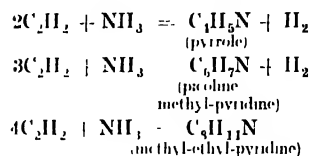
<sup>4</sup> Erdmann and Kolbner, *Zeitsch. angew. Chem.*, 1898, 18, 48.

<sup>5</sup> Bone and Coward, *Trans. Chem. Soc.*, 1908, 93, 1203.

<sup>6</sup> Meyer and Tanzen, *Ber.*, 1912, 45, 1609; 1913, 46, 3183.

<sup>7</sup> Tschitschibabin, *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 703.

or chromic oxide, heated slightly above 300° C., pyridine bases result thus :

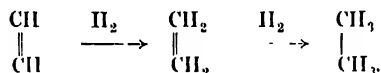


Sulphur may be incorporated within the molecule by the use of hydrogen sulphide or sulphur vapour ; thus thiophene,  $\text{C}_4\text{H}_4\text{S}$ , or its homologues may be produced.

Such reactions will account for the presence of heterocyclic compounds containing nitrogen and sulphur among the products of the dry distillation of natural petroleum if this is derived from a mineral source.

*Additive Reactions.* One molecule of acetylene can combine with 2 and with 4 hydrogen atoms or their equivalent, forming respectively ethylene and ethane or their derivatives.

Nascent hydrogen, or hydrogen gas through the catalytic agency of platinum-black or finely divided nickel,<sup>1</sup> converts acetylene into ethylene and ethane :



Platinum-black induces these reactions at atmospheric temperature, ethane resulting when there is excess of hydrogen, ethylene when excess of acetylene. When finely divided nickel is employed at 180° C. or above, polymerisation accompanies addition of hydrogen, and the products resemble natural petroleum.

The halogens combine with acetylene with decreasing readiness from chlorine to iodine, giving rise to halogen derivatives of ethylene and ethane.

Acetylene combines with chlorine, sometimes with explosive violence, forming acetylene dichloride or dichloroethylene,  $\text{CHCl} \cdot \text{CHCl}$ , and acetylene tetrachloride or tetrachlorethane,  $\text{CHCl}_2 \cdot \text{CHCl}_2$ . According to Mouneyrat<sup>2</sup> a mixture of chlorine and acetylene, when exposed to diffused daylight, forms acetylene tetrachloride without explosion, but the presence of oxygen or of a gas capable of liberating oxygen causes an explosion. Acetylene forms with  $\text{SbCl}_5$  the crystalline compound  $\text{C}_2\text{H}_2 \cdot \text{SbCl}_5$ , which on heating decomposes into  $\text{C}_2\text{H}_2\text{Cl}_2$  and  $\text{SbCl}_3$ . Chavanne<sup>3</sup> states that acetylene dichloride consists of two isomides separable by fractional distillation, and boiling at 49° C. and 60.2° C.

With bromine acetylene forms  $\text{C}_2\text{H}_2\text{Br}_2$  and  $\text{C}_2\text{H}_2\text{Br}_4$ , with iodine  $\text{C}_2\text{H}_2\text{I}_2$ , known in two stereoisomeric forms.<sup>4</sup> Acetylene slowly absorbs halogen hydride,  $\text{HX}$ , producing  $\text{CH}_3 \cdot \text{CHX}$  and  $\text{CH}_2 \cdot \text{CHX}_2$ ; and when sparked with nitrogen forms  $\text{HCN}$ .

<sup>1</sup> Sabatier and Senderens, *Compt. rend.*, 1900, 131, 40; 1902, 134, 1185

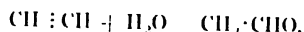
<sup>2</sup> Mouneyrat, *Bull. Soc. chim.*, 1898, [iii], 19, 451

<sup>3</sup> Chavanne, *Compt. rend.*, 1912, 154, 776

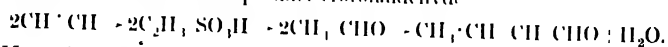
<sup>4</sup> Keiser, *Amer. Chem. J.*, 1899, 21, 261

Acetylene combines with cuprous chloride to form the white solids  $C_2H_2 \cdot CuCl$  and  $C_2H_2 \cdot 2CuCl$ . The former substance is soluble in water, but is obtained from absolute alcoholic solution at  $0^\circ C$ .<sup>1</sup>

Water combines with acetylene under the influence of catalysts to form acetaldehyde.



Concentrated sulphuric acid slowly absorbs acetylene, forming the sulphonic acid  $C_2H_2 \cdot SO_3H$ , which by hydrolysis yields acetaldehyde, and also its condensation product crotonaldehyde.<sup>2</sup>



Mercuric oxide, bromide, and other salts are also efficient catalysts, producing aldehyde in the cold.

**Halacetylenes.**—Substituted, as distinct from additive, halogen derivatives of acetylene are known. Monochloroacetylene,  $CCl \cdot CH$ , is an explosive gas obtained by the action of barium on dichloroacetylene,  $CCl_2 \cdot CH \cdot COOH$ . Monobromoacetylene,  $CBr \cdot CH$ , obtained by the action of alcoholic potash on acetylene dibromide,  $CHBr \cdot CHBr$ , is a spontaneously inflammable gas. Mono-iodoacetylene  $CI \cdot CH$ , is obtained by boiling the potassium salt of iodopropionic acid,  $CI \cdot CH \cdot COOK$ , with water. All three halogen derivatives can also be obtained by the decomposition of the corresponding halogen propionic acids.

The mercuric derivatives  $Hg(C \cdot CCl)_2$  and  $Hg(C \cdot CBr)_2$  have been prepared.<sup>3</sup>

Symmetrical di-iodoacetylene,  $CI \cdot CI$ , formed when iodine acts on silver acetylide, decomposes at  $78^\circ C$ . Asymmetrical di-iodoacetylene,  $CI_2 \cdot C$ , containing bivalent carbon, is said to be formed by the action of sodium hypiodite on acetylene.<sup>4</sup> According to Biltz,<sup>5</sup> however, there is no ground for assuming the existence of asymmetrical "acetylidene" derivatives, there being thus only one iodine derivative, viz.  $CI \cdot CI$ .

**Action of Acetylene on Metals.**—Pure, moist acetylene attacks nickel and copper, and the crude moist gas attacks zinc, lead, brass, nickel, phosphor-bronze, and copper. Copper is attacked rapidly, showing an increase in weight of 80 to 90 per cent. in six months. The product is black and non-explosive, and does not give acetylene with acids. In consequence of this action acetylene should not be brought in contact with copper tubes, but tubes conveying it should be tinned.<sup>6</sup>

**Metallic Derivates of Acetylene.**—The proportion of carbon to hydrogen in acetylene is so large that this hydrocarbon behaves as a feeble acid. It is not, however, sufficiently ionised in aqueous solution to show an acid reaction, its strength being only about 1/4000th that of carbonic acid, and its ionisation 1/10th that of water.<sup>7</sup> In consequence of this property salts of acetylene can be prepared in presence of water only when they are insoluble and may thus be precipitated;

<sup>1</sup> Manchot, Withers, and Obregge, *Annalen*, 1912, 387, 257.

<sup>2</sup> Schroeter, *Annalen*, 1898, 393, 114.

<sup>3</sup> Holmann and Kunreuther, *Ber.*, 1909, 42, 1232.

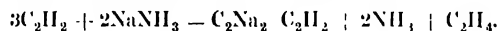
<sup>4</sup> Sabaneff, *Annalen*, 1875, 178, 118.

<sup>5</sup> Biltz, *Ber.*, 1913, 46, 143.

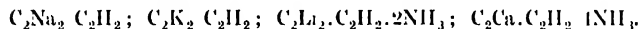
<sup>6</sup> Roekleben and Scheiber, *Chem. Zeit.*, 1915, 39, 42.

<sup>7</sup> Biltz, *Zeitsch. physikal. Chem.*, 1902, 40, 535.

otherwise they will be hydrolysed by water, and must be prepared in the dry way. Thus calcium carbide, prepared in the dry way, is hydrolysed into base and acid in the familiar preparation of acetylene:  $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$ . Nevertheless the increase in the solubility of acetylene in water brought about by the addition of alkali may indicate the formation of small quantities of salts in solution.<sup>1</sup> Alkali and alkaline earth carbides are formed when acetylene is passed into solutions of the metals in liquid ammonia, *i.e.* into solutions of metal-ammoniums (*e.g.*  $\text{NaNH}_2$ ).<sup>2</sup> Hydrogen carbides are first formed, *e.g.*  $\text{C}_2\text{HNa}$ , or more probably  $\text{C}_2\text{Na}_2 \cdot \text{C}_2\text{H}_2$ , the liberated hydrogen converting some of the acetylene into ethylene, thus:



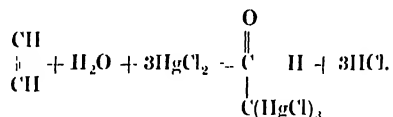
The following compounds have thus been obtained:



All these compounds decompose when heated, leaving the carbides  $\text{C}_2\text{Na}_2$ ,  $\text{C}_2\text{K}_2$ ,  $\text{C}_2\text{Li}_2$ ,  $\text{C}_2\text{Ca}$ . The molecular conductivity of  $\text{NaHC}_2$  in liquid ammonia is of the same order as that of sodium acetate.<sup>3</sup>

Insoluble silver and cuprous acetylides (or carbides)  $\text{C}_2\text{Ag}_2$  and  $\text{C}_2\text{Cu}_2$  are precipitated when acetylene is led into ammoniacal solutions of silver and cuprous salts. These compounds give off acetylene on treatment with acids, but are explosive when dry. The formation of cuprous acetylide, which is dark red, serves as a test for acetylene gas. The most sensitive cuprous solution for this test is made by saturating copper sulphate solution with sodium chloride, warming, and adding sodium hydrogen sulphite until the green colour disappears. A few drops of ammonia increase the sensitiveness of the reagent.<sup>4</sup>

Mercuric acetylide,  $\text{C}_2\text{Hg}$ , is formed when acetylene is passed into an alkaline solution of mercuric oxide, but acetylene reacts with an aqueous solution of mercuric chloride, thus<sup>5</sup>:



The trichloromercuric acetaldehyde is a precipitate which is decomposed by concentrated hydrochloric acid into aldehyde and mercuric chloride. This reaction explains the catalytic action of mercuric salts in bringing about the conversion of acetylene into aldehyde. A mixture of magnesium acetylide and allylide is formed when magnesium powder reacts with acetylene at  $450^\circ \text{C}$ .<sup>6</sup>

*Oxidation of Acetylene.*—Acetylene is oxidised to acetic acid when it is passed through solutions of hydrogen peroxide, persulphuric acid, permonosulphuric acid, or a salt of one of these acids in presence of

<sup>1</sup> Biltz et al., *loc. cit.*

<sup>2</sup> Moissan, *Compt. rend.*, 1898, 127, 911.

<sup>3</sup> Skossarewsky, *Compt. rend.*, 1914, 159, 769.

<sup>4</sup> Llorens, *Anal. Fis. Quim.*, 1912, 10, 139, also 1913, 11, 320.

<sup>5</sup> K. A. Hofmann, *Ber.*, 1898, 31, 2212, 2783; 1904, 37, 4459. Biltz and Mumm, *Ber.*, 1904, 37, 4417.

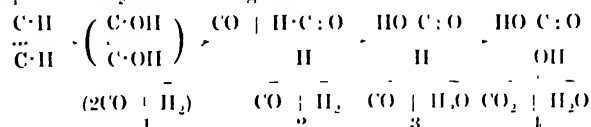
<sup>6</sup> Novák, *Ber.*, 1909, 42, 4209.

mercury or a mercury compound.<sup>1</sup> It may also be oxidised to acetic acid electrolytically.<sup>2</sup>

**Combustion of Acetylene.**—Acetylene ignites in contact with air at 480° C., and may be set fire to by means of red-hot carbonaceous matter. It burns with a flame which when suitably regulated is white and intense. The luminosity of acetylene when burnt at the rate of 5 cubic feet per hour is equal to 210 candle-power, while that of coal-gas equals from 11 to 18 candle-power. In order to burn acetylene without separation of carbon special burners have been constructed, in which the gas issues from two nozzles so made that air mixes with it as in the Bunsen burner. The two jets of gas then impinge upon each other obliquely, and produce a small, intense flame which does not smoke. The temperature of the acetylene flame is higher than that of coal-gas, and the temperature of the oxy-acetylene blowpipe flame approximates to that of the electric arc (3500° C.). The oxy-acetylene flame is used for the autogenous welding of steel and the cutting of steel plates.

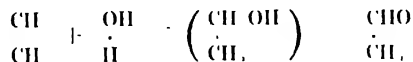
Acetylene requires about twelve times its volume of air for complete combustion, and shows a wider range of explosibility when mixed with air than any other gas, since mixtures containing between 3 and 82 per cent. of acetylene explode.<sup>3</sup>

The slow combustion of acetylene has been studied by Bone and Andrew.<sup>4</sup> These observers find that interaction between acetylene and oxygen, sealed up together in a glass vessel at atmospheric temperature, begins at 250° C., proceeds rapidly at 300° C., and becomes explosive from 350° to 375° C. The process of combustion of acetylene is essentially similar to that of methane, ethane, and ethylene, and consists primarily in the incorporation of oxygen within the molecule rather than the preferential oxidation of either carbon or hydrogen. The whole process is represented by the following scheme:



The separation of carbon, which occurs in an acetylene flame, is not a part of the process of combustion of this hydrocarbon, but is due to thermal decomposition of an excess over that required by the equation  $\text{C}_2\text{H}_2 + \text{O}_2 \rightarrow 2\text{CO} + \text{H}_2$ .

Hot porcelain promotes the catalytic formation of acetaldehyde, thus:



which may then produce  $\text{CH}_3 \cdot + \text{CO}$

There is no polymerisation to benzene in the presence of oxygen below the ignition-point.

<sup>1</sup> Farbenfabriken vorm. F. Bayer & Co. (French Patent 167,515), *J. Soc. Chem. Ind.*, 1914, 33, 830.

<sup>2</sup> *Ibid.* (French Patent 167,778), *J. Soc. Chem. Ind.*, 1914, 33, 830.

<sup>3</sup> Clowes, *B. A. Report*, 1896; see also De la pue, *Eighth Int. Cong. App. Chem.*, 1912,

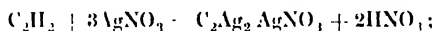
4, 25.

<sup>4</sup> Bone and Andrew, *Trans. Chem. Soc.*, 1905, 87, 1232.



**Physiological Action of Acetylene.**—Acetylene is much less poisonous than carbon monoxide, and even less poisonous than coal-gas. This is because the compound it forms with haemoglobin is unstable and easily decomposed by aeration.

**Estimation of Acetylene.** Acetylene may be estimated gravimetrically by causing it to react with ammoniacal cuprous solution, collecting the precipitated cuprous acetylide,  $C_2Cu_2$ , and converting this into the sulphide,  $Cu_2S$ , which is weighed. It may also be estimated volumetrically by titrating the nitric acid produced in the reaction<sup>1</sup>:



and gasometrically by absorbing it in a solution of ammoniacal silver chloride,<sup>2</sup> in which ethylene is almost insoluble.

### COAL-GAS

**History.**—Coal-gas was first described by Stephen Hales in 1726, and first manufactured by William Murdoch at Redruth, Cornwall, in 1792. In 1798 Murdoch lighted with gas the foundry of Messrs. Boulton and Watt at Soho, Birmingham, and in 1802 the Peace of Amiens was celebrated by an illumination in the same place. In 1803 La Moravian named Winsor demonstrated gas-lighting at the Lyceum in Piccadilly; in 1808 Murdoch lighted Messrs. Phillips and Lee's cotton-mill at Manchester with gas; in 1807 part of Pall Mall was similarly lighted; in the following year a gas company was incorporated in London, and the lighting of the capital with gas became general in 1812, whilst in 1815 the publication of Accum's *Practical Treatise on Gas Lighting* marked the full establishment of the gas industry. Paris was first lighted with gas in the latter year.

The chemical investigation of coal-gas was carried out by Dr. William Henry, and the development of plant is largely due to Samuel Clegg.

**Destructive Distillation of Coal.**—The nature of the products of the destructive distillation of bituminous coal, in absence of air, depends largely upon the temperature at which the process is carried out. When such coal is heated to 450°–500° C. it yields gas and only vapours consisting chiefly of paraffin hydrocarbons. Between 700° and 800° C. the residue evolves more gas consisting chiefly of hydrogen. Further heating of the paraffin hydrocarbons decomposes them into hydrogen and methane, together with some ethane and ethylene; whilst contact of these gases with the hot retort causes further splitting off of hydrogen and condensation of the nuclei into benzene, toluene, naphthalene, and anthracene, which are contained in the tar. Thus the raising of the temperature promotes more and more dissociation of hydrocarbons, the final result of which would be complete separation into carbon and hydrogen.

Some of the nitrogen of the coal remains in the coke, some appears as pyridine and quinoline in the tar, the rest as ammonia in ammoniacal liquor, as hydrocyanic acid and free nitrogen.

The oxygen of the coal is converted into steam, which condenses

<sup>1</sup> Chevascelon, *Compt. rend.*, 1897, 125, 215.

<sup>2</sup> Tucker and Moody, *J. Amer. Chem. Soc.*, 1901, 23, 671.

with ammonia as ammoniacal liquor or appears as CO or CO<sub>2</sub>; some of the sulphur remains in the coke, the rest forms volatile compounds which condense in the tar or appear as CS<sub>2</sub> or H<sub>2</sub>S, some of which combines with ammonia in the ammoniacal liquor and some remains in the gas.

*The Process of Carbonisation*—The retorts in which the coal is heated were originally made of iron but are now of fire-clay. When horizontal they are C-shaped, 20 ft. long and 21 × 16 in. in cross section, and hold a charge of 11 cwt., which fills the retort to the depth of 11 in. The number of retorts in a furnace may vary from two to eighteen; they are heated by producer gas, and carbonisation takes about twelve hours, the temperature of the retort rising to 1100° C., though the interior of the charge does not reach this temperature. A ton of Newcastle coal yields 12,500 cubic feet of gas and 110 lb. of tar, which on distillation leaves 77 lb. of pitch, whilst the ammoniacal liquor yields 7 lb. of ammonia. The remaining coke is 65–70 per cent. of the coal.

The retorts may be closed at one end or open so as to admit of charging from both ends; sometimes they are inclined at an angle of 30° with the horizontal, so that coal is introduced at the top and coke removed at the bottom. Sometimes the retorts are vertical and are completely filled with coal, so that the hot surface to which the gas is exposed is reduced to a minimum, and the quality of the gas maintained by the prevention of an excessive production of tar.

With the continuous employment of cannel and richly bituminous coal the available supplies of these varieties gradually diminished, until, about 1890, it became customary to enrich the gas made from the poorer kinds of coal by adding carburetted water-gas, *i.e.* water-gas containing vapourised mineral oil, and also to increase the yield of gas at the expense of illuminating power by the employment of a higher temperature of carbonisation, and then to compensate by oil-enrichment.

About this time the meandescut gas mantle was introduced, and the need for gas of high illuminating power ceased. Consequently the addition of carburetted water-gas to coal-gas has largely been discontinued, and in cases where this gas is still employed it possesses approximately the same illuminating power as the coal-gas.

*Products of Destructive Distillation*—The volatile products from the coal pass from the retort by a wide pipe, bent twice and leading vertically downwards to the *hydraulic main*, where by partial cooling imperfect separation into the three following constituents takes place:

- (i) impure coal-gas,
- (ii) ammoniacal liquor
- (iii) tar.

The ammoniacal liquor forms an aqueous layer above the tar, and consists of an aqueous solution of ammonia, hydrogen sulphide, and carbon dioxide. From it most of the ammonia of commerce is prepared, whilst from the tar many important and complex "coal-tar products" are obtained.

The crude coal-gas still, however, contains ammonia, tar, sulphur compounds and other substances, from which it is purified by a series of operations.

**Purification of Coal-gas.**—When it leaves the hydraulic main the gas has a temperature of about 50°–60° C., and contains besides tar the following impurities, which must be removed :

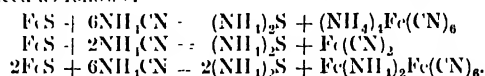
Ammonia	0.70	1.40	per cent. by volume.
Hydrogen cyanide	0.05	0.15	.. ..
Sulphuretted hydrogen	0.9	1.70	.. ..
Carbon disulphide	0.02	0.04	.. ..

The gas is cooled by passage through a series of vertical tubular *condensers*, which may be cooled with water. Here much of the remaining tar is condensed, though sometimes there is a special *tar-extractor*, where the remaining particles of this substance, which constitute "tar-fog," are removed mechanically. The efficient extraction of naphthalene at this stage is very important. The gas next passes through the *exhauster*, which is a pump by which the pressure and consequent flow of the gas are regulated. Then follow the *scrubbers*, which are towers filled with broken bricks, coke, or slanting boards. Down these towers water is sprayed to meet the up-coming gas and remove from it the last traces of ammonia. At the same time some sulphuretted hydrogen and carbon dioxide are removed and form ammonium sulphide and carbonate. Mechanical rotary washers have now largely replaced the scrubbers. Owing, however, to the trouble of recovering ammonia from dilute solution, processes for the direct absorption of this gas by acid, without the intermediate formation of ammoniacal liquor, are now being introduced.

**Extraction of Cyanide.** The extraction of cyanide from coal-gas is a comparatively recent industry rendered important by the demand for cyanides in gold-mining, and also by the recognition of the corrosive action of hydrocyanic acid on iron and steel.

Cyanide is extracted in the form either of ferrocyanide or thiocyanate by one or other of the following processes :

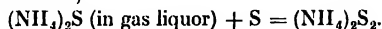
- (i) **Ferrocyanide process (Bueh) :** Previous to entering the scrubbers for removal of ammonia the gas reacts with ferrous sulphate solution or ferrous sulphide suspended in water, ferrocyanides being produced as follows :



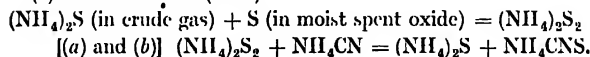
Sometimes the gas reacts with alkali and ferrous carbonate and hydroxide, hydrogen sulphide being at the same time absorbed. (Foulis process).

- (ii) **Thiocyanate process :**

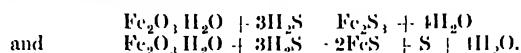
(a) **British Cyanides Co. :** The gas passes through ammoniacal liquor containing suspended sulphur, whereby ammonium polysulphide and thiocyanate are successively produced; the sulphur may, however, be derived from moist spent oxide (Williams) :



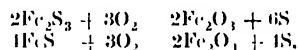
(b) **P. E. Williams (1909) :**



*Removal of Sulphuretted Hydrogen.*—Sulphuretted hydrogen is removed from coal-gas by a dry absorption method. The absorbent may be: (i) lime; (ii) ferric oxide, as Irish or Dutch bog ore, precipitated hydroxide, or “Lux” from bauxite; (iii) manganese dioxide, as Weldon mud. Ferric oxide is the most general absorbent, and is most active when precipitated. It is placed on wooden grids contained in a series of cast-iron boxes or *purifiers*, through which the gas passes; and the following reactions take place:



When the oxide is “spent,” it is removed from the purifiers, moistened, and exposed to the air, so that oxidation takes place as follows:

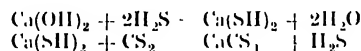


and thus the “spent oxide” becomes “revivified.”

The revivified oxide is used over and over again, whilst sulphur accumulates within it until 50–60 per cent. is present. It is then employed for the manufacture of sulphuric acid. Sometimes a little air is added to the coal-gas previous to the absorption of sulphuretted hydrogen, in order that oxidation may proceed simultaneously. In this way the ferric oxide lasts longer without requiring to be changed.

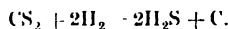
As it leaves the purifiers the gas should not discolour a strip of lead acetate paper when passed for three minutes through a vessel containing it. The gas will then contain not more than one volume of sulphuretted hydrogen in ten million.

*Removal of Carbon Disulphide.*—Carbon disulphide vapour present in coal-gas is not absorbed by oxide of iron, and its removal, though desirable, is not always carried out. The only known absorbent for carbon disulphide is calcium hydrosulphide, which is produced from slaked lime when the latter is employed to remove sulphuretted hydrogen from the gas. The reactions may be represented as follows, calcium thiocarbonate being formed:



Calcium thiocarbonate is an objectionable and almost useless by-product, and on this account the process is often omitted.

An alternative process for eliminating carbon disulphide consists in passing the coal-gas at 230° C. over fire-clay surfaces impregnated with metallic nickel. The following reaction takes place with the hydrogen of the coal-gas:



The hydrogen sulphide thus produced is absorbed by ferric oxide, and the carbon can be burned off from the nickel surface, which is thus renewed for further use.<sup>1</sup>

After purification the gas passes through the meter-house to the holders, whence it is distributed to the consumers.

<sup>1</sup> Clowes *J. Soc. Chem. Ind.*, 1916, 35, 581

**Composition of Coal-gas.**—The composition of coal-gas varies with the kind of coal employed and the sort of retort in which it is heated. The following figures are typical:

	Average Composition	Ordinary Bituminous Coal <sup>1</sup>	
		Horizontal Retorts	Vertical Retorts
Hydrogen, per cent.	13.0-55.0	11.0-52.0	18.0-57.0
Methane	25.0-35.0	27.0-36.0	26.0-32.0
Carbon monoxide	1.0-11.0	6.0-10.0	6.0-12.0
Unsaturated hydrocarbons	2.5-5.0	3.0-4.5	2.5-4.0
Nitrogen	2.0-12.0	3.0-10.0	2.0-6.0
Carbon dioxide	0.0-3.0	1.5-3.0	1.0-3.0
Oxygen	0.0-1.5	0.1-0.8	0.0-0.3

## CARBON AND THE HALOGENS

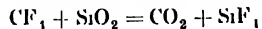
### CARBON HALIDES

Numerous halides of carbon are theoretically capable of existence. Not only may successive hydrogen atoms of the many hydrocarbons be replaced by halogen atoms to form substitution derivatives, each series of which ends in a carbon halide, but mixed halide derivatives may also exist. The formation of halogen derivatives of methane by substitution, viz. the series of compounds  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , has already been noticed, as well as that of additive compounds, such as  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{C}_2\text{H}_2\text{Cl}_4$ , by ethylene and acetylene respectively.

The present study will be limited to halides containing a single carbon atom, i.e. to the four compounds  $\text{CF}_4$ ,  $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CI}_4$ .

• **Carbon Tetrafluoride** (*Tetrafluoromethane*),  $\text{CF}_4$ .—Fluorine is the only halogen that will unite readily with carbon. Moissan <sup>2</sup> has shown that in fluorine gas purified lampblack becomes incandescant, and wood-charcoal takes fire spontaneously, but that it is necessary to heat the denser forms of amorphous carbon to 50°-100° C. to induce combination; whilst graphite and gas-carbon react with fluorine only at a red heat, and diamond is unaffected at any temperature.

Carbon tetrafluoride results from the substitution of fluorine for hydrogen or halogen in methane or any of its halogen substitution products, but is best prepared by passing the vapour of carbon tetrachloride over silver fluoride heated in a metallic tube to 195°-200° C. Carbon tetrafluoride is a gas at ordinary temperatures and pressures; it is liquefied at 20° C. under four atmospheres, and at -15° C. under one atmosphere pressure. It is slightly soluble in water, and very soluble in alcohol and ether; it reacts with the silica of heated glass, thus:



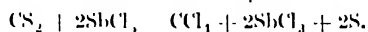
<sup>1</sup> The figures that follow, and some other information in this section, are derived from lectures on "Chemistry in Gas Works," delivered by W. J. A. Butterfield before the Institute of Chemistry (1913).

<sup>2</sup> Moissan, *Compt. rend.*, 1890, **110**, 276

and with heated sodium forms fluoride with separation of carbon. It is absorbed by alcoholic potash, being gradually converted into a mixture of potassium fluoride and carbonate.<sup>1</sup>

It is noteworthy that no complex acid,  $\text{H}_2\text{CF}_6$ , analogous to  $\text{H}_2\text{SiF}_6$ , has been described; and indeed that carbon tetrafluoride, like the tetrachloride, is unacted on by water.

**Carbon Tetrachloride** (*Tetrachloromethane*),  $\text{CCl}_4$ . *Preparation*.—Carbon tetrachloride is the final chlorination product of methane, but it is generally prepared by the action of chlorine on carbon disulphide through the catalytic agency of a chlorine-carrier. Thus Hofmann<sup>2</sup> dissolved antimony trichloride in carbon disulphide, and passed dry chlorine through the solution. The trichloride became pentachloride, which then reacted with the carbon disulphide, thus,



Other catalysts which may be employed are chloride of bromine,<sup>3</sup> chloride of iodine,<sup>4</sup> phosphorus pentachloride,<sup>5</sup> molybdenum pentachloride,<sup>6</sup> and aluminum chloride.<sup>7</sup>

Carbon tetrachloride is also prepared in several ways by the action of chlorine on carbon in the electric furnace.<sup>8</sup>

*Physical Properties*. Carbon tetrachloride is a colourless liquid which smells like chloroform: it does not mix with water, though it appears to form an unstable hydrate; it dissolves in many organic liquids, and is itself a useful solvent. The properties of mixtures of ethyl alcohol, carbon tetrachloride, and water have been examined by T. H. Hill.<sup>9</sup> Its density at 0° C. is 1.5947,<sup>10</sup> and at 32.5° C. is 1.5683;<sup>11</sup> its boiling-point is 76.65° C. at 760 mm. pressure.<sup>12</sup> The critical temperature is 282.51° C., and the critical pressure 57.57 atm.<sup>13</sup> The specific heat of liquid carbon tetrachloride rises from 0.2010 at 0° C. to 0.2031 at 70° C.; that of the vapour falls from 0.140 at 0° C. to 0.115 at 70° C.<sup>14</sup> Solid carbon tetrachloride is amorphous,<sup>15</sup> the melting-points of the three modifications being 28.6° C., 23.77° C., 21.2° C. The depression constant, when camphor or ethyl benzoate is used as solute, is found to be 47 or 48.<sup>12</sup>

*Chemical Properties*. When the vapour of carbon tetrachloride is passed through a red-hot tube chlorine is split off and the compounds  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{Cl}_6$  result. From the latter compound, hexachloroethane, trichloroacetic acid is formed by aqueous hydrolysis in the presence of

<sup>1</sup> Moissan, *Compt. rend.*, 1890, 110, 951.

<sup>2</sup> Hofmann, *J. Chem. Soc.*, 1861, 14, 62.

<sup>3</sup> Müller and Crump, *Chem. News*, 1866, 356, 154. Weber, *Bull. Soc. chim.*, 1867, [n], 7, 187. Morel, *Compt. rend.*, 1877, 84, 1460.

<sup>4</sup> Friedl and Silva, *Bull. Soc. chim.*, 1872, [n] 17, 537.

<sup>5</sup> Rathke, *Techn. J. chem.*, 1870, p. 57.

<sup>6</sup> Hentschel, *J. prakt. Chem.*, 1877, [n] 36, 306. Moenneviat, *Bull. Soc. chim.*, 1898,

[n], 19, 262. Bricau, *J. Pharm. chim.*, 1908, [vi], 28, 110.

<sup>8</sup> Michalske and Lyon, *J. Soc. Chem. Ind.*, 1903, 22, 1298; Michalske, *Chem. Zentr.*, 1904, 1, 1069; Michalske and Dillington, *J. Soc. Chem. Ind.*, 1906, 25, 509; Matthews and Dillington, *ibid.*, 1906, 25, 559. Maywald, *ibid.*, 1907, 26, 1253.

<sup>9</sup> Hill, *Trans. Chem. Soc.*, 1912, 101, 2167.

<sup>10</sup> Thorpe, *Trans. Chem. Soc.*, 1880, 37, 141.

<sup>11</sup> Joseph, *Trans. Chem. Soc.*, 1915, 107, 1.

<sup>12</sup> Moles, *Anal. Fis. Quim.*, 1912, 10, 70.

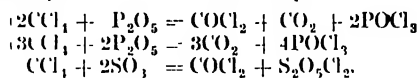
<sup>13</sup> Hannay, *Proc. Roy. Soc.*, 1880, 30, 183; 1881, 33, 319.

<sup>14</sup> Mills and MacRae, *J. Physical Chem.*, 1911, 15, 54.

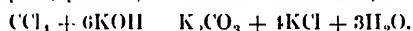
<sup>15</sup> Tammann, *Rec. Annalen*, 1898, 66, 489.

sunlight, and this is reduced by nascent hydrogen to acetic acid. Since carbon tetrachloride can be obtained from its elements by way of carbon disulphide, this compound marks a stage in the synthesis of acetic acid.

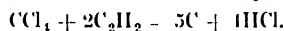
Chemically, carbon tetrachloride is the chloride of the hypothetical orthocarbonic acid,  $\text{C}(\text{OH})_4$ , just as the analogous silicon compound is the chloride of orthosilicic acid,  $\text{Si}(\text{OH})_4$ . Although carbon tetrachloride, unlike the silicon halide and acid chlorides in general, is not attacked by water at atmospheric temperature, this halide is capable of some reactions which reveal its relation to carbonic acid. When heated with oxygen and water under pressure at  $250^\circ \text{C}$ , it yields phosgene gas,  $\text{COCl}_2$ , and carbon dioxide,  $\text{CO}_2$ , and a similar change is brought about by certain acidic oxides,<sup>1</sup> e.g.:



When heated with alcoholic potash carbon tetrachloride is completely hydrolysed, yielding carbonate and chloride, thus:



It reacts with acetylene, with liberation of finely divided carbon, thus:

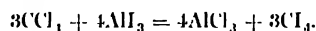


Its vapour readily chlorinates various oxides, and may on this account be used in mineral analysis.<sup>2</sup>

**Carbon Tetrabromide** (*Tetrabromomethane*),  $\text{CBr}_4$ . Carbon tetrabromide is prepared similarly to the chloride by the action of bromine on carbon disulphide, iodine being in this case the halogen-carrier. A mixture<sup>3</sup> of 2 parts of carbon bisulphide, 11 parts of bromine, and 3 parts of iodine is heated in a sealed tube for forty-eight hours at  $250^\circ \text{C}$ , and the product distilled when cold with sodium hydroxide solution. Carbon tetrabromide is a solid, and crystallises from alcohol in white, glistening tablets having an ethereal smell; it has a density of 3.12, melts at  $92.5^\circ \text{C}$ , and boils under atmospheric pressure with partial decomposition at  $189.5^\circ \text{C}$ , whilst under 50 mm. pressure the boiling-point is  $101^\circ \text{C}$ .

Solid carbon tetrabromide exists in two enantiotropic forms, the transition temperature between which is  $16^\circ$ – $17^\circ \text{C}$ .<sup>4</sup>

**Carbon Tetraiodide** (*Tetraiodomethane*),  $\text{CI}_4$ .—This compound results from the interchange of chlorine and iodine when carbon tetrachloride reacts with aluminum<sup>5</sup> or boron<sup>6</sup> iodide. It may be prepared by dropping a solution of the tetrachloride in carbon bisulphide on to aluminum iodide at  $0^\circ \text{C}$ .:



Lantenois<sup>7</sup> prepares this compound by heating lithium iodide with excess of carbon tetrachloride in a vacuum in a sealed tube at  $90^\circ$ – $92^\circ \text{C}$ .

<sup>1</sup> Gustavson, *Jahresber.*, 1872, p. 216

<sup>2</sup> Camboulives, *Compt. rend.*, 1910, 150, 175, 221

<sup>3</sup> Bolus and Groves, *Trans. Chem. Soc.*, 1870, 23, 154, 161, 1871, 24, 773.

<sup>4</sup> Schwartz-Rooreboom, *Phasenlehr.* 1901, i, 127. Rothmund, *Zeitsch. physikal. Chem.*, 1899, 29, 664

<sup>5</sup> Gustavson, *Compt. rend.*, 1874, 78, 882

<sup>6</sup> Moissan, *Compt. rend.*, 1891, 113, 19. <sup>7</sup> Lantenois, *Compt. rend.*, 1913, 156, 1385.

for five days. The best solvents for carbon tetraiodide are benzene, acetone, and carbon disulphide. It crystallises in dark red, regular octahedra, having a density of 4.32. When exposed to air it begins to decompose, producing carbon dioxide and iodine; it has no melting-point, but from 50° C. onwards decomposes into its elements. Carbon tetraiodide is attacked by hydrogen at 100° C., the chief product being iodoform; alcoholic potassium hydroxide at 30°-40° C. also produces iodoform. Oxygen forms carbonyl iodide with liberation of iodine even in the dark. Carbon tetraiodide is estimated by means of its reaction with 20 per cent. silver nitrate solution, carbon monoxide and dioxide being evolved in the proportion of 3 to 1 by volume.<sup>1</sup>

#### CARBON OXYHALIDES

Just as the carbon tetrahalides,  $CX_4$ , may be regarded as the halides—or the halohydrides—of orthocarbonic acid,  $C(OH)_4$ , so the oxyhalides,  $COX_2$ , are the halides of metacarbonic acid,  $CO(OH)_2$ .

**Carbon Oxychloride** (*Carbonyl Chloride*, *Phosgene*),  $COCl_2$ . The name phosgene was given to this gas by J. Davy,<sup>2</sup> who in 1811 observed its generation by the action of light upon a mixture in equal volumes of carbon monoxide and chlorine. This phenomenon is analogous to that of the union of hydrogen and chlorine under the influence of light; the union of carbon monoxide and chlorine has, however, this advantage, that it is accompanied by a diminution of volume at constant pressure, or of pressure at constant volume; consequently the course of the reaction can be conveniently traced.

It was observed by Bunsen and Roscoe<sup>3</sup> that when a mixture of hydrogen and chlorine is exposed to light the amount of hydrogen chloride produced per unit time increases for a certain period, after which the rate of combination becomes proportional to the amount of gas remaining uncombined; and to the action during this preliminary period these observers gave the name "photochemical induction."

Dyson and Harden<sup>4</sup> observed a similar phenomenon with carbon monoxide and chlorine, and attributed it to the specific action of light on chlorine, and Chapman and Gee<sup>5</sup> came to a similar conclusion, though the interpretation they gave of the induction process is quite different from that of Bunsen and Roscoe. These observers have found that small quantities of nitric oxide, ozone, and nitrogen chloride inhibit the photochemical action, i.e. extend the period of so-called "induction," during which this action is slow, and almost entirely prevent it. Thus they attribute photochemical action to the use chlorine can make of absorbed and transformed light energy to effect union with carbon monoxide or hydrogen, before such energy is degraded to the form of ineffective heat. The inhibiting action of extraneous gases is then due to the hastening of the process of energy degradation, and the consequent loss of efficiency by the chlorine.

Carbonyl chloride is best prepared by passing its constituent gases separately into a large glass balloon exposed to sunlight, and thence

<sup>1</sup> Lantenou, *Compt. rend.*, 1913, 156, 1629.

<sup>2</sup> Davy, *Phil. Trans.*, 1812, 114.

<sup>3</sup> Bunsen and Roscoe, *Phil. Trans.*, 1857, 335.

<sup>4</sup> Dyson and Harden, *Trans. Chem. Soc.*, 1903, 83, 201; see also Wildermann, *Zetsch. physikal. Chem.*, 1903, 42, 259.

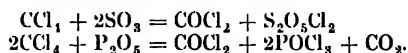
<sup>5</sup> Chapman and Gee, *Trans. Chem. Soc.*, 1911, 99, 1726.



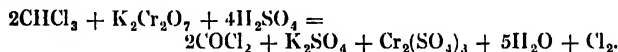
## CARBON AND ITS ALKYL

through a second balloon similarly exposed. The chlorine should be in excess, and may afterwards be absorbed by means of metallic antimony; whilst the carbonyl chloride may be purified by liquefaction in a freezing mixture. Carbon monoxide and chlorine may also be made to combine through the influence of electric sparks, animal charcoal, or spongy platinum.

Carbonyl chloride results from the action of acidic oxides such as  $\text{P}_2\text{O}_5$  and  $\text{SO}_3$  or  $\text{H}_2\text{S}_2\text{O}_7$  upon carbon tetrachloride.<sup>1</sup> Sulphur trioxide reacts at  $100^\circ \text{C}$ ., phosphoric oxide at  $200^\circ \text{C}$ .



Carbonyl chloride may also be prepared by the oxidation of chloroform by chromic acid, when 20 parts of chloroform, 400 of sulphuric acid, and 50 of potassium dichromate are heated together on the water-bath<sup>2</sup>:



Another method of formation of carbonyl chloride, which takes place in the electric furnace, is represented by the following equation:



*Physical Properties.*—Carbonyl chloride is a colourless gas with a pungent taste and suffocating smell. Its density under normal conditions is 3.505 (theory requires 3.468). It is easily condensed to a liquid having a density<sup>4</sup> of 1.432 at  $0^\circ \text{C}$ ., and boiling at  $8.2^\circ \text{C}$ . under 756 mm pressure; the solid<sup>5</sup> melts at  $-118^\circ \text{C}$ . The heat of formation from amorphous carbon at constant pressure  $[\text{C}, \text{O}, \text{Cl}_2]$  is, according to Thomsen,<sup>6</sup> 55,140 calories, and from diamond 44,100 calories (Berthelot<sup>7</sup>). The gas dissolves in water and alcohol, undergoing decomposition.

*Chemical Properties.*—The dissociation of carbonyl chloride according to the reaction  $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$  has been studied by Bodenstein and Durrant,<sup>8</sup> who passed the gas or an equimolecular mixture of carbon monoxide and chlorine through a heated tube, and analysed the issuing gas. Thus they found the following percentages decomposed at the given temperatures:

Temperature $^\circ \text{C}$ .	503	553	603	800
Per cent. decomposed	67	80	91	100

Thence they calculated the heat of formation of carbonyl chloride from carbon monoxide and chlorine to be about 23,000 calories, whereas Berthelot<sup>9</sup> obtained the value 18,800 calories, and Thomsen 26,140 calories. According to Coehn and Becker<sup>10</sup> the dissociation equilibrium of carbonyl chloride is affected by ultraviolet light.

<sup>1</sup> Gustavson, *Ber.*, 1872, 5, 30.

<sup>2</sup> Emmerling and Lengyel, *Ber.*, 1869, 2, 547; *Annalen*, 1869, *Suppl.*, 7, 105

<sup>3</sup> Michalske, *Zeitsch. angew. Chem.*, 1906, 19, 1775

<sup>4</sup> Michalske, *ibid*

<sup>5</sup> Erdmann, *Annalen*, 1908, 362, 148.

<sup>6</sup> Thomsen, *Ber.*, 1883, 16, 2619.

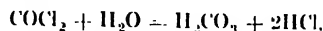
<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1870, [v], 17, 129.

<sup>8</sup> Bodenstein and Durrant, *Zeitsch. physikal. Chem.*, 1908, 61, 437.

<sup>9</sup> Berthelot, *Ann. Chim. Phys.*, 1870, [v], 17, 129

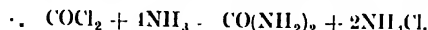
<sup>10</sup> Coehn and Becker, *Ber.*, 1910, 43, 130

Carbonyl chloride is the chloride of carbonic acid, and as such reacts with water thus :

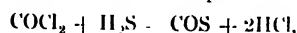


the carbonic acid then decomposing into carbon dioxide and water.

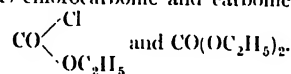
With ammonia there is produced carbamide or urea.



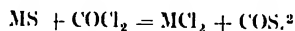
and with hydrogen sulphide carbonyl sulphide, thus :



whilst alcohol yields chlorocarbonyl and carbonyl esters :

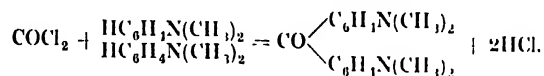


Certain metals when heated in carbonyl chloride form chlorides, liberating CO, e.g. :  $\text{COCl}_2 + \text{Zn} = \text{ZnCl}_2 + \text{CO}$ ; and numerous oxides are converted into chlorides when heated in a stream of carbonyl chloride.<sup>1</sup> Mineral sulphides are also converted into chlorides by the reaction :



Natural phosphates and silicates also yield chlorides when heated with carbonyl chloride vapour.<sup>2</sup>

Carbonyl chloride is employed in the manufacture of certain synthetic dye-stuffs, e.g. it reacts with dimethylamine in the presence of aluminium chloride to form tetramethyldiamidobenzophenone :



**Carbon Oxybromide** (*Carbonyl Bromide*).  $\text{COBr}_2$ . Carbon oxybromide is obtained in an impure condition by the interaction of phosphorus or boron tribromide and carbon oxychloride, and also in small quantities by the union of carbon monoxide and bromine in presence of aluminium bromide, or under the influence of the silent electric discharge. The rate of combination of the dry gases is very slow; probably no reaction would take place between them in the complete absence of water.<sup>4</sup> Carbon oxybromide is best obtained<sup>5</sup> by slowly dropping concentrated sulphuric acid into carbon tetrabromide heated to about  $160^\circ \text{C}$ ., and redistilling the product after contact with metallic antimony :



Carbon oxybromide is a colourless, mobile, fuming liquid of density 2.45 at  $15^\circ \text{C}$ . It boils at  $64^\circ$ - $65^\circ \text{C}$ . with slight decomposition; it is more stable towards water than carbonyl chloride; like the latter, it reacts with dimethyl aniline to form dye-stuffs.

<sup>1</sup> Chauvenet, *Comp. rend.*, 1911, 152, 87.

<sup>2</sup> Chauvenet, *ibid.*, 1911, 152, 1250.

<sup>3</sup> Barlot and Chauvenet, *Compt. rend.*, 1913, 157, 1153.

<sup>4</sup> Piva, *Gazzetta*, 1915, 45, 1, 219.

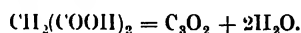
<sup>5</sup> Bartal, *Annalen*, 1906, 345, 334.

## CARBON AND THE OXYGEN GROUP

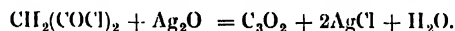
## OXIDES OF CARBON

The two important oxides of carbon, carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, were for many years the only known oxides. In 1873 the oxide C<sub>3</sub>O<sub>2</sub> was obtained by Brodie<sup>1</sup> by subjecting carbon monoxide to prolonged electric discharges; and in 1877 Berthelot<sup>2</sup> produced C<sub>3</sub>O<sub>2</sub> by heating Brodie's oxide to 300°–400° C. In 1906 Diels and Wolf<sup>3</sup> obtained C<sub>3</sub>O<sub>2</sub>, a substance which has aroused much interest. Mellitic anhydride is C<sub>12</sub>O<sub>6</sub><sup>4</sup>; an unsuccessful attempt has been made to prepare dicarbon dioxide,<sup>5</sup> CO : CO.

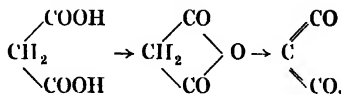
**Carbon Suboxide, C<sub>3</sub>O<sub>2</sub>.**—Carbon suboxide is among the products of the distillation of ethyl malonate at 300° C. and a pressure of 12 mm. over a large excess of phosphoric oxide. Other malonic esters and the esters of related acids, as well as malonic acid itself,<sup>6</sup> can similarly be made to yield the suboxide by a reaction which is essentially



The suboxide is freed from ethylene and carbon dioxide, formed at the same time, by allowing the distillate, condensed by liquid air, to boil at atmospheric temperature; the residue is then vaporised, and collected at –60° C. Carbon suboxide is also formed by the interaction of malonyl chloride with silver, lead, or zinc oxide, thus:



Silver oxalate or malonate may be employed in place of the oxide.<sup>7</sup> Carbon suboxide is a colourless, mobile, refractive liquid having an odour which resembles that of acetaldehyde and mustard oil, and is poisonous. It boils at 7° C. under 761 mm. pressure, and its vapour density corresponds to the formula C<sub>3</sub>O<sub>2</sub>. It burns with a bright blue smoky flame, producing carbon dioxide according to the reaction: C<sub>3</sub>O<sub>2</sub> + 2O<sub>2</sub> = 3CO<sub>2</sub>. The liquid oxide slowly changes at atmospheric temperature into a dark red solid of approximately the same composition, whose aqueous solution is cosm-red. This change, which is partly one of decomposition, is rapid at 37° C. and instantaneous at 100° C. The oxide combines with water to form malonic acid, and with hydrogen chloride, ammonia, and aniline to form malonyl chloride, malonamide, and malonanilide respectively. Its discoverers therefore regarded it as the second anhydride of malonic acid, thus:



<sup>1</sup> Brodie, *Annalen*, 1873, 169, 270.

<sup>2</sup> Berthelot, *Ann. Chem. Phys.*, 1877, [v], 10, 72.

<sup>3</sup> Diels and Wolf, *Ber.*, 1906, 39, 689.

<sup>4</sup> Meyer and Steiner, *Ber.*, 1913, 46, 813.

<sup>5</sup> Staudinger and Anthos, *Ber.*, 1913, 46, 1426.

<sup>6</sup> Diels and Meyerheim, *Ber.*, 1907, 40, 355.

<sup>7</sup> Staudinger and St. Berez, *Ber.*, 1908, 41, 4461.

Michael<sup>1</sup> considers the oxide to be the lactone of  $\beta$ -hydroxy-propionic acid, and thus to have the constitution  $\text{C} \begin{matrix} \nearrow \text{O} \\ \searrow \text{CO} \end{matrix}$ ; but this

view is not acceptable to Diels and Meyerheim,<sup>2</sup> who adhere to the "dioxallene" formula,  $\text{O} : \text{C} : \text{C} : \text{C} : \text{O}$ ; and Diels and Lalm<sup>3</sup> have shown that the suboxide behaves as a ketene, giving with formic acid

the additive compound:

$$\begin{array}{c} \text{HOOC} \quad \text{COOH} \\ \diagdown \quad \diagup \\ \text{C} : \text{C} : \text{C} \\ \diagup \quad \diagdown \\ \text{HIO} \quad \text{OH} \end{array}$$

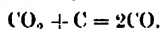
Berthelot<sup>4</sup> claimed that the term "carbon suboxide" is properly applied to the compounds discovered previously by Brodie and himself, and therefore cannot legitimately be used for the compound  $\text{C}_3\text{O}_2$ .

#### CARBON MONOXIDE

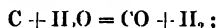
(*Carbomic oxide*)

Formula, CO

**Occurrence.**—Carbon monoxide is found amongst the gases evolved from active volcanoes, and occurs in small quantity in some minerals, and in diamantiferous earth at Kimberley.<sup>5</sup> This gas is also present in coal-gas to the extent of 6-12 per cent, and is formed simultaneously with carbon dioxide in the combustion of carbon,<sup>6</sup> as well as by the reduction of the latter gas when it passes over red-hot carbon:



Hence carbon monoxide is formed in a coke fire, on the top of which it burns with a pale flame; and it is produced in various metallurgical operations in which coal or coke is used as fuel, as, for instance, in the blast-furnace. It is an important constituent of water-gas, made by passing steam over carbon at  $1000^\circ \text{C}$  :



and of producer gas formed by passing air, together sometimes with steam, through red-hot carbonaceous material. Carbon monoxide is an intermediate product, also, in the combustion of hydrocarbons, and is found in the interconal gases of the Bunsen flame.

**History.**—Carbon monoxide, or carbomic oxide, as it is sometimes rather erroneously called, was discovered in 1776 by Lussone,<sup>7</sup> who obtained it during the reduction of zinc oxide by charcoal. On account of the blue flame with which it burns, this gas was at first mistaken for hydrogen, and its production was cited by Priestley in support of that version of the phlogiston theory which supposed that metallic calces contain water, and that inflammable air, *i.e.* hydrogen, is phlogisticated

<sup>1</sup> Michael, *Ber.*, 1906, 39, 1915

<sup>2</sup> Diels and Meyerheim, *Ber.*, 1907, 40, 355

<sup>3</sup> Diels and Lalm, *Ber.*, 1908, 41, 3426

<sup>4</sup> Berthelot, *Compt. rend.*, 1906, 142, 533

<sup>5</sup> Ramsay and Travers, *Proc. Roy. Soc.*, 1897, 60, 442

<sup>6</sup> Rhead and Wheeler, *Trans. Chem. Soc.*, 1912, 101, 831, 846.

<sup>7</sup> Lussone, *Mém. Paris Acad.*, 1776.

## CARBON AND ITS ALLIES

water. In 1800 Cruikshank showed that when the gas burns it produces no water, but an equal volume of carbon dioxide; and in 1802 Clément and Desormes confirmed Cruikshank's observation, and also showed that the same gas is produced when carbon dioxide is passed over red-hot charcoal. In his *New System of Chemical Philosophy* (1808) Dalton showed that "carbomic oxide is a binary compound consisting of one atom of charcoal and one of oxygen . . ." and that "carbomic acid is a ternary compound . . . consisting of one atom of charcoal and two of oxygen." Thus the nature and composition of carbon monoxide were definitely established.

**Preparation.**—The methods available for the preparation of carbon monoxide fall into four categories:

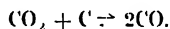
- A. Partial oxidation of carbon.
- B. Partial reduction of carbon dioxide.
- C. Dehydration of formic acid and its derivatives or of other oxyacids.
- D. Electrolytic decomposition of a suitable oxyacid.

A. Carbon is oxidised to carbon monoxide when excess of it is heated with zinc oxide, ferric oxide, manganese dioxide, or other reducible oxide. The reactions are, however, of little importance for the preparation of the gas.

B. Carbon dioxide may be reduced to carbon monoxide in various ways

- (1) By red-hot carbon.

It is well known that red-hot charcoal reduces carbon dioxide according to the reaction:



That the reaction is reversible, carbon monoxide dissociating at high temperature into carbon and carbon dioxide, was shown in 1861 by Deville.<sup>1</sup> The matter was further investigated by Sir Lothian Bell,<sup>2</sup> in 1869, who showed that finely divided metals promote the decomposition of carbon monoxide; and by Boudouard,<sup>3</sup> in 1902, who employed iron, nickel, and cobalt as catalysts, and showed that the equilibrium ratio  $\text{CO} : \text{CO}_2$  is a function of temperature, the reaction beginning at about 600° C.

The effect of temperature on the equilibrium represented by the above equation has been studied by Rhead and Wheeler,<sup>4</sup> who have obtained the results given in the table on the opposite page.

The equation of equilibrium for the reaction is

$$-\frac{19,500}{T} + \log_e \frac{c_1^2}{c_2} = k$$

where  $T$  is absolute temperature,  $c_1$  and  $c_2$  are molecular concentrations of carbon monoxide and dioxide respectively, and  $k$  is a constant, the mean value for which is 20.39, the gases being left approximately at atmospheric temperature, when equilibrium is attained. The effect of pressure on the equilibrium has also been studied by Rhead and Wheeler.<sup>5</sup>

<sup>1</sup> Deville *Compt. rend.*, 1864, 59, 873, 1865, 60, 317.

<sup>2</sup> Bell, *J. Chem. Soc.*, 1869, 22, 203.

<sup>3</sup> Boudouard, *Ann. Chim. Phys.*, 1901, [vii], 24, 5.

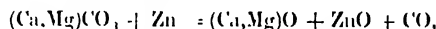
<sup>4</sup> Rhead and Wheeler, *Trans. Chem. Soc.*, 1910, 97, 2181.

<sup>5</sup> Rhead and Wheeler, *ibid.*, 1911, 99, 1140.

Temperature ° C.	Per cent by volume	
	CO <sub>2</sub>	CO
850	6.23	93.77
900	2.22	97.78
950	1.32	98.68
1000	0.59	99.41
1050	0.37	99.63
1100	0.15	99.85
1200	0.06	99.94

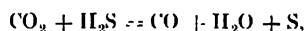
Gautier<sup>1</sup> has shown that carbon monoxide is not appreciably dissociated into carbon dioxide and carbon at the melting-point of lava (1250° C.), and therefore may exist in the pyrosphere of the earth.

(2) Metallic zinc may also be employed to reduce carbon dioxide to the monoxide. Thus carbon monoxide is formed when zinc filings are heated with chalk or magnesite.

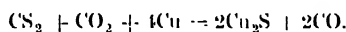


and likewise when carbon dioxide is passed over zinc dust heated just short of redness in a glass tube.

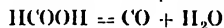
Carbon dioxide may also be reduced by means of hydrogen sulphide \* thus :



or by leading the vapour of carbon disulphide with carbon dioxide over red-hot copper<sup>2</sup>:

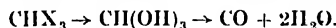


C. The dehydration of formic acid represented by the reaction

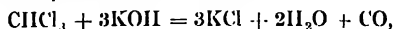


may be carried out by heating the acid or a suitable salt such as sodium formate with concentrated sulphuric acid, when pure carbon monoxide gas is evolved.

Chloroform, bromoform and iodoform, being derivatives of orthoformic acid, may also be made to yield carbon monoxide by suitable means, the course of the reaction being represented thus :



According to Desgrez,<sup>3</sup> chloroform yields carbon monoxide when treated with cold aqueous potash solution, thus :



the reaction being accelerated by light. Bromoform is decomposed more slowly in this way, and iodoform not at all.

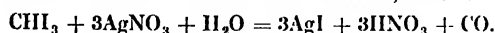
<sup>1</sup> Gautier, *Compt. rend.*, 1910, 150, 1383.

<sup>2</sup> Kohler, *Ber.*, 1883, 11, 265.

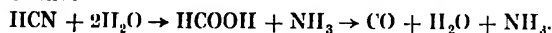
<sup>3</sup> Edvart, *Chem. News*, 1885, 52, 183.

<sup>4</sup> Desgrez, *Compt. rend.*, 1897, 125, 780.

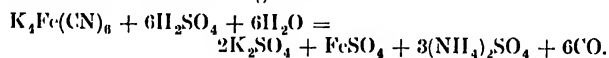
Silver nitrate, however, aids the decomposition of iodoform on account of the formation of insoluble silver iodide, thus<sup>1</sup>:



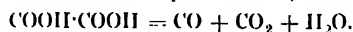
Hydrocyanic acid, or formonitrile, yields carbon monoxide by the reactions:



Thus potassium cyanide yields carbon monoxide when heated with concentrated sulphuric acid; but it is usual to prepare this gas by heating finely powdered potassium ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , with eight to ten times its weight of concentrated sulphuric acid, the water in the acid and in the salt being sufficient for the reaction:

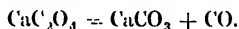


Other carboxylic acids besides formic acid, such as tartaric and citric acids, yield carbon monoxide among the products of their decomposition by means of sulphuric acid; and oxalic acid yields carbon monoxide and carbon dioxide in equal volumes, thus:

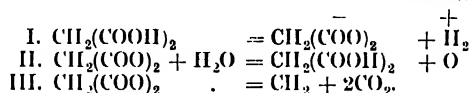


It is therefore convenient to prepare carbon monoxide by heating oxalic acid with concentrated sulphuric acid, and absorbing the carbon dioxide by passing the gaseous mixture through a solution of caustic alkali.

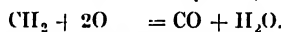
By an analogous reaction oxalates when heated yield carbon monoxide, leaving a residue of carbonate, as, e.g.:



D. Carbon monoxide is produced by the electrolysis of malonic acid, which according to Petersen<sup>2</sup> undergoes the following changes:



The nascent oxygen then oxidises methylene ( $\text{CH}_2$ ) thus:



**Physical Properties of Carbon Monoxide.**—Carbon monoxide is a colourless gas without taste or smell, which is very poisonous. Its density (air = 1) is 0.96702 (Ledue<sup>3</sup>) or 0.96716 (Rayleigh<sup>4</sup>). To the latter density the molecular weight 27.9989 corresponds, whilst CO requires M.W. = 28.002; therefore at atmospheric pressure carbon monoxide is practically an ideal gas. The molecular weight of CO is the same as that of nitrogen ( $\text{N}_2 = 28.02$ ); and in condensibility and other physical properties the two gases closely resemble each other.

The coefficient of expansion of carbon monoxide at atmospheric pressure is 0.0036667,<sup>5</sup> which is that for an ideal gas.

<sup>1</sup> Seubentrauch, *Zeitsch. Nahr. Genussm.*, 1898, S. 737.

<sup>2</sup> Petersen, *Zeitsch. physikal. Chem.*, 1900, 33, 699.

<sup>3</sup> Ledue, *Compt. rend.*, 1892, 115, 1072.

<sup>4</sup> Rayleigh, *Proc. Roy. Soc.*, 1897, 62, 204.

<sup>5</sup> Regnault, *Pogg. Annalen*, 1842, 57, 118.

Natterer<sup>1</sup> determined the diminishing compressibility of the gas at high pressures. Compressibility is expressed by the ratio  $\frac{p_0 v_0}{p v}$  where  $p_0 = 1$  atmosphere. Some of the values obtained are given in the following table.

$p$ , (atm.)	$\frac{p_0 v_0}{p v}$
77	1.000
204	0.965
408	0.900
515	0.810
629	0.727
814	0.623
1133	0.500
1716	0.366
2790	0.261

Carbon monoxide was liquefied by Cailliet<sup>2</sup> in 1877, and by Wroblewski and Olszewski<sup>3</sup> in 1883, who cooled the gas to  $-136^\circ \text{C}$ . in boiling ethylene and compressed it to 150 atmospheres. It forms a colourless liquid which boils at  $-193^\circ \text{C}$  (Wroblewski<sup>4</sup>) or  $-190^\circ \text{C}$ . (Olszewski<sup>5</sup>) under 1 atm. pressure, and forms a snowlike solid at  $-211^\circ \text{C}$  (Cailliet) or  $-199^\circ \text{C}$  (Wroblewski). The critical temperature and pressure of carbon monoxide, together with the constants  $a$  and  $b$  for van der Waals' equation, are:

Critical Temp., $^\circ \text{C}$	Critical Pressure	$a$	$b$	
$-141.1$	35.9 atm.	0.00275	0.001683	Wroblewski
$-139.5$	35.5 ..	0.00285	0.001723	Olszewski

The critical density<sup>6</sup> of carbon monoxide is 0.3110.

The densities of liquid carbon monoxide at different temperatures have been determined by Baly and Donnan.<sup>7</sup> They are expressed by the formula.

$$d = 0.8558 - 0.0042 (T - 68), \quad T = \text{abs. temp.}$$

The specific heat of carbon monoxide between  $99^\circ \text{C}$ . and  $23^\circ \text{C}$ . is 0.2425,<sup>8</sup> and the ratio  $\frac{C_p}{C_v}$  is approximately 1.40,<sup>9</sup> the value for a diatomic gas.

<sup>1</sup> Natterer, *Pogg. Annalen*, 1855, 94, 436

<sup>2</sup> Cailliet, *Compt. rend.*, 1877, 85, 815

<sup>3</sup> Wroblewski and Olszewski, *Compt. rend.*, 1883, 96, 1110, 1226

<sup>4</sup> Wroblewski, *Compt. rend.*, 1881, 98, 985

<sup>5</sup> Olszewski, *Compt. rend.*, 1881, 98, 706

<sup>6</sup> Cardoso, *Arch. Sci. phys. nat.*, 1915, [iv], 39, 103

<sup>7</sup> Baly and Donnan, *Trans. Chem. Soc.*, 1902, 81, 913.

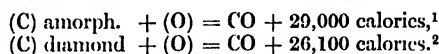
<sup>8</sup> Wiedemann, *Pogg. Annalen*, 1876, 157, 1

<sup>9</sup> Wullner, *Wied. Annalen*, 1878, N.F., 4, 331; Cazim, *Ann. Chim.*, 1862, [iii], 56, 206; Leduc, *Compt. rend.*, 1898, 127, 659. See also Scheel and Heuse *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 44.



## CARBON AND ITS ALLIES

The heat of combustion ( $\text{CO}_2$ ) is 88,200 calories, and the heats of formation are as follow:



Carbon monoxide is very slightly soluble in water; its solubility at different temperatures is represented by the following equation<sup>3</sup>:

$$c = 0.032784 - 0.008009t + 0.000015872t^2.$$

Its solubility in other solvents has been investigated by Just,<sup>4</sup> Skirrow,<sup>5</sup> and Christoff.<sup>6</sup>

**Chemical Properties of Carbon Monoxide.**—Carbon monoxide is an unsaturated compound which unites with oxygen, either free or combined, to form carbon dioxide; and also with various other substances under suitable conditions.

*Union of Carbon Monoxide with Oxygen.*—Carbon monoxide can reduce compounds containing oxygen not only at high temperature, as in metallurgy,<sup>7</sup> but also in some cases at low temperatures.

For example, silver oxide and yellow mercuric oxide oxidise carbon monoxide at atmospheric temperature,<sup>8</sup> as well as permanganic acid<sup>9</sup> and ammoniacal silver nitrate; whilst chromic acid reacts similarly at 100° C., and crystallised iodic anhydride at 90° C., being thereby reduced to iodine.<sup>10</sup>

The reaction between carbon monoxide and gaseous oxygen, i.e. the process of combustion of carbon monoxide, has been the subject of much investigation.

Combination of these gases can be brought about by passing the mixed gases over moist phosphorus.<sup>11</sup> Probably hydrogen peroxide or ozone plays a part in the reaction; and either of these substances has the power of oxidising carbon monoxide in presence of palladium.<sup>12</sup> In presence of a heated palladium wire the union of carbon monoxide with oxygen is complete at 300° C.<sup>13</sup> Combination between the two gases also takes place gradually under the influence of the silent electric discharge.<sup>14</sup>

The influence of temperature upon the degree of combination between carbon monoxide and oxygen has been studied by Hélier,<sup>15</sup> who obtained the following results:

Temperature ° C.	195	302	408	500	566	600	689	855
Per cent. combination	0.13	0.44	3.03	6.2	14.43	21.14	46.38	65.0

<sup>1</sup> Thomsen, *Thermochemische Untersuchungen* (Dr J Traube), Enke, (Stuttgart), 1906, p. 195.

<sup>2</sup> Berthelot, *Ann. Chim. Phys.*, 1878, [v], 13, 14; 1880, 20, 260, 1881, 23, 177; Berthelot and Matignon, *Ann. Chim. Phys.*, 1893, [vi], 30, 555.

<sup>3</sup> Henrich, *Zeitsch. physikal. Chem.*, 1892, 9, 435.

<sup>4</sup> Just, *Zeitsch. physikal. Chem.*, 1901, 37, 342.

<sup>5</sup> Skirrow, *Zeitsch. physikal. Chem.*, 1902, 41, 139.

<sup>6</sup> Christoff, *Zeitsch. physikal. Chem.*, 1906, 55, 622.

<sup>7</sup> Vide Charpy, *Compt. rend.*, 1909, 148, 560.

<sup>8</sup> Colson, *Compt. rend.*, 1901, 132, 467.

<sup>9</sup> Just and Kauko, *Zeitsch. physikal. Chem.*, 1913, 82, 71.

<sup>10</sup> Nicloux, *Compt. rend.*, 1898, 126, 746; Gautier, *Compt. rend.*, 1898, 126, 793, 931;

Phillips, *Zeitsch. anorg. Chem.*, 1891, 6, 243.

<sup>11</sup> Leeds, *Ber.*, 1879, 12, 1836; Baumann, *Ber.*, 1884, 17, 283.

<sup>12</sup> Traube, *Ber.*, 1882, 15, 2854; 1883, 16, 123.

<sup>13</sup> Richardt, *Zeitsch. anorg. Chem.*, 1904, 38, 69.

<sup>14</sup> Mixter, *Amer. J. Sci. (Sill.)*, 1897, [iv], 4, 51; A. de Hemptune, *Zeitsch. physikal. Chem.*, 1903, 46, 18.

<sup>15</sup> Hélier, *Ann. Chim. Phys.*, 1897, [vii], 10, 521.

## CARBON AND ITS COMPOUNDS

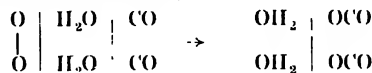
These figures are of relative value only, as true equilibrium was not attained. The kinetics of the reaction between these two gases at  $570^{\circ}\text{C}$ . has been studied by Kuhl,<sup>1</sup> who found that the order in which they were introduced into the reaction vessel in presence of moisture, and whether or not carbon dioxide was originally present, had much influence on the velocity of the reaction. Bodenstein and Ohlmer<sup>2</sup> have observed that the reaction is catalytically accelerated by quartz-glass.

The influence of moisture in promoting the combination of these two gases is noteworthy. A mixture of dried carbon monoxide and oxygen is not exploded by a spark,<sup>3</sup> though a mixture of the moist gases is so exploded. If a dried mixture is contained in a long tube into one end of which a little moisture is introduced, the moistened mixture will explode, but the flame dies out as it reaches the dried gases.<sup>4</sup> Dried carbon monoxide and oxygen will unite in the path of an electric spark<sup>5</sup>; the reaction, however, is reversible, and a limit is reached when the rates of combination and decomposition are equal.<sup>6</sup> The dried gases also combine, without explosion or flame, when in contact with a hot platinum wire.<sup>7</sup>

It is clear from the above statements that whilst the presence of water is not always necessary to the union of carbon monoxide and oxygen, its presence greatly facilitates the combustion of the former gas. Thus carbon monoxide burns in moist air with a pale blue flame, but such a flame is extinguished when it is plunged into dry air.<sup>8</sup>

Not only water-vapour itself, but other substances capable of forming water-vapour by combustion, such as hydrogen, hydrogen sulphide and hydrocarbons, promote the combustion of carbon monoxide; and continued addition of water-vapour to a mixture of carbon monoxide and oxygen accelerates the velocity of explosion until about 4.5 per cent. has been added.<sup>9</sup>

Various explanations of this catalytic action of water-vapour have been given. According to Armstrong<sup>10</sup> the two gases, which are inert in the pure state, require "the formation of a conducting system in which electrolysis can occur," or, according to a later exposition,<sup>11</sup> oxidation takes place "in a circuit composed of the oxidisable substance, conducting water and oxygen." Briefly, Armstrong's view may be represented by the following scheme:



in which the elements of water appear to be partitioned between oxygen and carbon monoxide. Against this view is the fact that when dry

<sup>1</sup> Kuhl, *Zeitsch. physikal. Chem.*, 1903, 44, 385.

<sup>2</sup> Bodenstein and Ohlmer, *Zeitsch. physikal. Chem.*, 1905, 53, 160.

<sup>3</sup> Dixon, *B. 1. Report*, 1880, 503.

<sup>4</sup> Dixon, *Chem. News*, 1882, 46, 151.

<sup>5</sup> L. Meyer, *Ber.*, 1886, 19, 1099; Beketoff, *Bull. Acad. Petrograd*, 2, 175.

<sup>6</sup> Dixon and Lowe, *Trans. Chem. Soc.*, 1885, 47, 571.

<sup>7</sup> Dixon and Lowe, *ibid.*

<sup>8</sup> Traube, *Ber.*, 1885, 18, 1890.

<sup>9</sup> Dixon, *Phil. Trans.*, 1893, A, 184, 111.

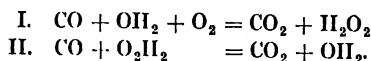
<sup>10</sup> Armstrong, *Proc. Roy. Soc.*, 1886, 40, 287; *Trans. Chem. Soc.*, 1886, 49, 112; *Presidential Address*, *Trans. Chem. Soc.*, 1895.

<sup>11</sup> Armstrong, *Trans. Chem. Soc.*, 1903, 83, 1088.

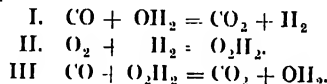
## CARBON AND ITS ALLIES

cyanogen is exploded with excess of oxygen or burnt in a Smithells separator, whilst the final products are carbon dioxide and nitrogen, carbon monoxide is formed as an intermediate product, and subsequently burns to carbon dioxide in the complete absence of water-vapour.

Traube<sup>1</sup> has put forward the theory that the water molecules yield their oxygen to carbon monoxide at the same time that the remaining hydrogen appropriates a molecule of oxygen to form hydrogen peroxide, thus :

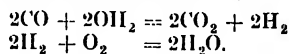


Carbon monoxide is, however, directly oxidised by steam at high temperature; and Mendeléeff,<sup>2</sup> who accepted Traube's theory with regard to hydrogen peroxide, consequently gave the following equations, which illustrate his belief that reactions between equal volumes of gases precede all others :



Traube's theory of the formation of hydrogen peroxide is, however, denied by Wieland,<sup>3</sup> who supports Armstrong's views.

Dixon,<sup>4</sup> who has reviewed the various theories which have been advanced to account for the inertness of dry carbon monoxide in presence of dry oxygen, advances the suggestion that the dissociation of carbon dioxide at the temperature at which carbon monoxide and oxygen would combine accounts for the non-appearance of the former gas; but that in the presence of steam carbon monoxide is oxidised thereby, the liberated hydrogen recombining with oxygen to form steam, which is stable at the temperature of the combustion, thus :



It cannot be said, however, that the function of water-vapour in promoting the combustion of carbon monoxide has been definitely established.

It may be mentioned that according to Gautier<sup>5</sup> interaction between carbon monoxide and water-vapour takes place at 1200°–1250° C. The reactions of carbon monoxide with hydrogen, water-vapour, and iron and its oxides have been studied by Gautier and Clausmann, and their bearing upon volcanic and geological phenomena and the origin of petroleum has been discussed.<sup>6</sup>

*Addition Products of Carbon Monoxide.*—Besides uniting with oxygen, carbon monoxide, as an unsaturated compound, forms addition products with a number of other substances. The fact that this gas combines with chlorine under the influence of light to form carbonyl chloride (q.v. p. 97), but not with bromine or iodine, has already been noticed.

<sup>1</sup> Traube, *Ber.*, 1883, 16, 123, 1885, 18, 1890

<sup>2</sup> Mendeléeff, *Principles of Chemistry*, 2nd Eng. edn., 1905, vol. i, p. 312.

<sup>3</sup> Wieland, *Ber.*, 1912, 45, 679

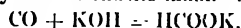
<sup>4</sup> Dixon, *Trans. Chem. Soc.*, 1896, 69, 774

<sup>5</sup> Gautier, *Compt. rend.*, 1906, 142, 1382

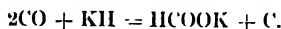
<sup>6</sup> Gautier, *Compt. rend.*, 1910, 150, 1564; Gautier and Clausmann, *Compt. rend.*, 1910, 151, 16, 355.

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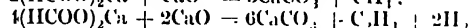
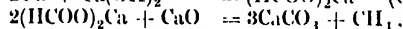
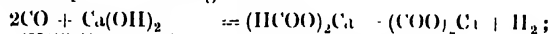
Combination with sulphur vapour to form carbonyl sulphide, COS, takes place at a red heat; hydrogen combines with carbon monoxide to produce formaldehyde under the influence of the silent electric discharge, but by the help of a catalyst such as metallic nickel reduces this gas to methane.<sup>1</sup> Alkali formate is produced by the absorption of carbon monoxide by heated caustic alkali<sup>2</sup>:



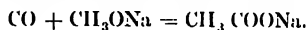
and also by the action of the gas on alkali hydride, carbon being separated thus:



By the interaction of lime and carbon monoxide between 350° C. and 400° C. considerable quantities of methane, ethylene, and hydrogen are formed by the following reactions<sup>3</sup>:



Carbon monoxide also reacts with sodium methoxide and its homologues at 160° C. to produce the sodium salt of the corresponding carboxylic acid<sup>4</sup>—

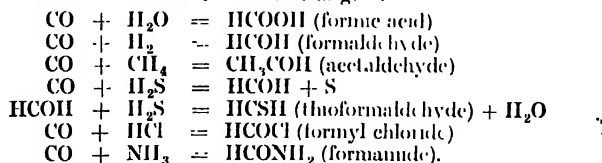


One of the most important additive reactions of carbon monoxide, since it is used in the volumetric estimation of this gas, is its combination with cuprous chloride. The conditions of this reaction have been studied by Manchot and Friend,<sup>5</sup> who find that the ratio Cu:CO determines the maximum limit of absorption—the compound  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ , which crystallises in colourless leaflets, being formed in all cases.

The absorption of carbon monoxide by a hydrochloric acid solution of cuprous chloride increases with decreasing concentration of hydrogen chloride, with lowering of temperature, with increasing concentration of cuprous chloride, and increasing pressure of carbon monoxide.

Ammonia, aniline, etc., may take the place of water in the compound  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ ; otherwise water is necessary. An alcoholic suspension of cuprous chloride, for example, does not absorb carbon monoxide. Cuprous hydroxide does not combine with carbon monoxide, but in presence of sodium hydroxide is reduced thereby to copper.

A number of interesting syntheses can be brought about by substituting carbon monoxide mixed with various other gases and vapours to the influence of the silent electric discharge<sup>6</sup>:



<sup>1</sup> Sarreau and Vieille, *Compt. rend.*, 1887, 105, 1225.

<sup>2</sup> Berthelot, *Ann. Chim. Phys.*, 1856, [iii], 46, 477, 1900, [vii], 21, 205.

<sup>3</sup> Vignon, *Bull. Soc. chim.*, 1911, [iv], 9, 18.

<sup>4</sup> Wohler, *Annalen*, 1860, 113, 358, *Lech, Annalen*, 1862, 124, 20, Berthelot, *Bull. Soc. chim.*, 1866, [ii], 5, 1.

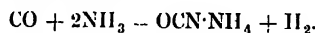
<sup>5</sup> Manchot and Friend, *Annalen*, 1908, 359, 100. See also vol. II (this series) under "Cuprous Salts."

<sup>6</sup> Losanitsch and Jovitschitsch, *Ber.*, 1897, 30, 135.

According to Kuhlmann,<sup>1</sup> however, ammonium cyanide is formed when carbon monoxide and ammonia are passed together over heated platinum-black :



but Jackson and Northall-Laurie<sup>2</sup> find that ammonium cyanate, which gives rise to urea, is formed thus :



Ultra-violet rays also cause combinations between carbon monoxide and other gases.<sup>3</sup>

When carbon monoxide itself is submitted to prolonged electric discharges one or more suboxides of carbon are produced (see p. 100).

**Compounds of Carbon Monoxide with Metals.—Metallic Carbonyls.**—In his Presidential Address before the Chemical Section of the British Association in 1896 Dr. Ludwig Mond described a carbide of nickel which he had observed to be formed on some nickel valves; and this observation led to the discovery in 1890 of a volatile compound of nickel and carbon monoxide: nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , whose formation and decomposition has proved of great practical value in the metallurgy of nickel.<sup>4</sup> The following carbonyls are known to exist<sup>5</sup>:  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}_2(\text{CO})_8$ ,  $[\text{Co}(\text{CO})_3]_n$ ,  $\text{Fe}(\text{CO})_5$ ,  $[\text{Fe}_2(\text{CO})_9]_n$ ,  $[\text{Fe}(\text{CO})_4]_n$ ,  $[\text{Mo}(\text{CO})_6]_n$ ,  $[\text{Ru}(\text{CO})_5]_n$ ; and they will be described under the corresponding metals. Their constitution is still a matter of conjecture.

A potassium carbonyl,  $\text{K}_2(\text{CO})_6$ , which is explosive, and was formed in the old Brunner process for the manufacture of potassium by heating potassium carbonate with carbon, is probably the potassium derivative of hexahydroxybenzene.

**Physiological Action of Carbon Monoxide.**—Carbon monoxide gas is very poisonous to man and animals. As early as 1716 the poisonous nature of the fumes arising from burning charcoal was recognised by F. Hoffmann.<sup>6</sup> Many deaths have been caused by breathing the gas arising from imperfectly burnt charcoal, or air mixed with coal-gas.

The poisonous action of carbon monoxide is generally supposed to be due to the formation with the hæmoglobin or red colouring-matter of the blood of a compound, carboxyhæmoglobin, which is much more stable than the compound oxyhæmoglobin which oxygen forms. Thus the activity of the blood as an oxygen-carrier is seriously or fatally inhibited. The absorption coefficient of blood for carbon monoxide is 0.022.<sup>7</sup> Blood becomes more purple by the absorption of carbon monoxide, and when diluted forty times shows an absorption spectrum containing two bands between the D and E lines, which much resembles that of oxygenated blood. The spectrum of the latter is, however, modified by the reducing action of ammonium sulphide or ammoniacal ferrotartrate, whilst that of blood containing carbon monoxide remains unchanged for several days after the addition of a reducing agent. The spectroscopic estimation of carbon monoxide in blood has been

<sup>1</sup> Kuhlmann, *Annalen*, 1841, 38, 62.

<sup>2</sup> Jackson and Northall-Laurie, *Trans. Chem. Soc.*, 1905, 87, 433.

<sup>3</sup> D Berthelot and Gaudechon, *Compt. rend.*, 1913, 157, 120.

<sup>4</sup> Mond, *Trans. Chem. Soc.*, 1890, 57, 749.

<sup>5</sup> Mond, Hertz, and Cowap, *Trans. Chem. Soc.*, 1910, 97, 798.

<sup>6</sup> Hoffmann, *Considerations on the Fatal Effects of the Vapour from Burning Charcoal*,

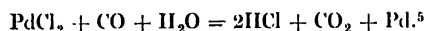
1716.

<sup>7</sup> Hufner, *Arch. exp. Pathol. Pharmac.*, 1902, 48, 87.

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elaborated by Hartridge.<sup>1</sup> According to Giocoso,<sup>2</sup> the theory that carbon monoxide poisons by replacing oxyhaemoglobin by carboxyhaemoglobin can no longer be maintained. Carbon monoxide appears to have no effect upon the germination of seeds or the action of ferments,<sup>3</sup> though it retards the catalytic action of finely divided platinum.<sup>4</sup>

**Detection and Estimation of Carbon Monoxide.** Carbon monoxide may be detected by its reducing action on metallic salt solutions, the most sensitive of which is palladous chloride. The gas containing carbon monoxide is passed through a dilute solution of palladous chloride, when metallic palladium is precipitated according to the reaction :



The reaction with blood serves for the detection of 0.25 per cent. of carbon monoxide in air.<sup>6</sup>

Carbon monoxide is generally estimated by the loss of volume consequent upon its absorption in an ammoniacal or hydrochloric acid solution of cuprous chloride.

The gas may also be estimated by combustion, or by oxidation by iodine pentoxide at 150° C., followed by titration of the carbon dioxide after absorption in baryta water. This method, which is due to Gautier,<sup>7</sup> has been elaborated by Levy.<sup>8</sup>

The quantity of carbon monoxide in a mixture of this gas with hydrogen and methane may be determined by fractional combustion when the mixture is passed over palladium-asbestos at a rate not exceeding 1 litre per hour, the carbon monoxide alone being oxidised ; and when a similar mixture is passed over copper oxide at 250° C. the methane is also unaffected.<sup>9</sup>

### CARBON DIOXIDE

(Carbonic Anhydride. Carbonic Acid Gas)

Formula  $\text{CO}_2$ . Molecular weight = 44.

**History.**—Carbon dioxide was first recognised by van Helmont, early in the seventeenth century, as a gas which differed in properties from air. This chemist showed that the gas is produced by acting on limestone and potashes with acids, by the burning of coal, and by the fermentation of wine and beer ; that it is contained in the stomach, in mineral waters, and in caves such as the Grotto del Cane, near Naples ; and that it possesses suffocating properties and extinguishes a flame. The name *gas sylvestre* was given by van Helmont to carbon dioxide, because the gas appeared to be uncondensable (*sylvestris* = wild). The first scientific investigation of carbon dioxide was made by Black in 1753, who in his "Experiments upon Magnesia-alba, Quicklime, and other Alkaline Substances" <sup>9</sup> showed that this substance is present

<sup>1</sup> Hartridge, *Proc. Roy. Soc.*, 1913, B, 86, 128.

<sup>2</sup> Giocoso, *Atti R. Acad. Torino*, 1904, 39, 421.

<sup>3</sup> Senter, *Zeitsch. physikal. Chem.*, 1905, 51, 694.

<sup>4</sup> Bredig, *Anorganische Fermente*, Leipzig, 1901, p. 58.

<sup>5</sup> Winkler, *Zeitsch. anal. Chem.*, 1889, 28, 275.

<sup>6</sup> Vogel, *Ber.*, 1878, 11, 235.

<sup>7</sup> Levy, *J. Soc. Chem. Ind.*, 1911, 30, 1437.

<sup>8</sup> Nesimeloff, *Zeitsch. anal. Chem.*, 1900, 48, 232.

<sup>9</sup> Black, *Edin. Phys. and Literary Essays*, 1755.

in a combined state in calcium and magnesium carbonates, whence it may be driven by heat or acids. On account of its presence in solid carbonates Black named this gas *fixed air*. Bergmann,<sup>1</sup> who in 1774 published an account of carbon dioxide, called it *acid of air* because of its presence in the atmosphere. Scheele and Priestley showed that in the burning of a candle fixed air took the place of dephlogisticated air; and Lavoisier, in 1775-6, established the chemical nature and composition of the gas by showing that it is produced when mercuric oxide is heated with carbon; whilst Dalton, in 1803, showed that "carbonic acid" contains twice as much oxygen combined with the same quantity of carbon as "carbonic oxide" does, and that these two gases furnish an example of the law of multiple proportions.

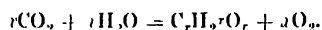
**Atmospheric and Terrestrial Carbon Dioxide.**—In the early ages of the earth's geological history the distribution of carbon dioxide was quite different from what it is now. Then the basic oxides of the earth's crust were combined mainly with silica, whilst the atmosphere was very rich in carbon dioxide. This was because the high temperature of the igneous rocks favoured combination with silica rather than with carbon dioxide. The displacement of carbon dioxide by silica on fusion of the latter with sodium carbonate illustrates the principle. With the aid of atmospheric aqueous vapour, however, a process of weathering of siliceous rocks commenced by which carbonates were formed, and silicic acid, silica, or silicates of less basic metals liberated. The weathering of felspar, by which potassium aluminium silicate is converted into potassium carbonate, aluminium silicate or kaolin, and free silica, is the most familiar example of this process. By the aid of rain, and consequent streams and rivers, these carbonates or bicarbonates were carried in solution to the sea.

Meanwhile the sea itself was receiving in solution much carbon dioxide directly from the atmosphere, continual interchange of this gas taking place between the two media. Partly by organic decomposition, but chiefly through the agency of marine organisms, the bicarbonates of calcium and magnesium were decomposed, and sedimentary rocks produced from the carbonates thus set free, while the free carbonic acid containing half the carbon dioxide originally removed from the air eventually returned this carbon dioxide to the air, which by means of circulation again became available for weathering. Thus carbon dioxide has been continuously removed from the air and stored up in the crust of the earth in the various forms of limestone rocks and coral reefs. So great has been the storage of carbon dioxide by this means that at the present day there is about thirty thousand times as much of this compound in the sedimentary rocks as in the atmosphere.

Simultaneously with this process a quite different agency was at work reducing the amount of carbon dioxide in the air. The green parts of plants, and especially their leaves, possess the power of decomposing atmospheric carbon dioxide in the presence of sunlight, retaining the carbon and returning the oxygen to the air. The chlorophyll, or green colouring-matter, of the leaves is associated with masses of protoplasm to constitute chlorophyll corpuscles or chloroplasts. The radiant energy absorbed by the colour is employed by this protoplasm

<sup>1</sup> Bergmann, *Opuscula*, 1774, i, 1, "De acido aereo."

to bring about a chemical change which may be represented by the equation :



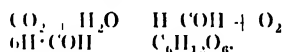
The significance and importance of this process of photosynthesis in the economy of nature can hardly be overestimated. First, the excessive amount of carbon dioxide originally present in the air was gradually replaced by oxygen; secondly, carbohydrate was produced, whence is derived food for man and beast; thirdly, energy was stored up—e.g. in coal—in the separation of carbon and oxygen, which again becomes available when the products are employed as fuel, and the carbon returns to the air as carbon dioxide. Thus the cycle

carbon dioxide → "organic" carbon → carbon dioxide

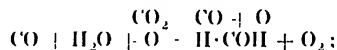
is completed. From the point of view of mass it provides the carbonaceous basis of living organisms; from the point of view of energy it furnishes the source of their activities.

The decomposition of atmospheric carbon dioxide by green plants was observed by Priestley, Senbier, and Ingenhousz before the close of the eighteenth century, and Mayer and Helmholtz showed the importance of the reaction as a means by which energy is stored. By throwing a continuous spectrum upon a filament of alga impregnated with bacteria which are stimulated to active movement only in presence of free oxygen, Englemann<sup>1</sup> proved that the energy absorbed from white light by chlorophyll is employed by the plant in photosynthesis. The zones of activity of the bacteria were found to coincide with the positions of the absorption bands of the chlorophyll spectrum.

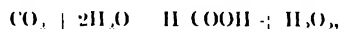
With regard to the actual process of carbon assimilation, Baeyer<sup>2</sup> advanced the theory that formaldehyde is the first product, and that this substance polymerises, thus:



According to Baeyer the first reaction takes place in two stages, thus:



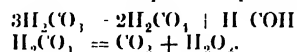
but Erlenmeyer<sup>3</sup> assumes the production of formic acid and hydrogen peroxide thus:



which then interact, giving formaldehyde, water, and oxygen, thus:



A somewhat different view was expressed by Bach<sup>4</sup> in the equations



Erlenmeyer's views find experimental support in the work of Usher and Priestley,<sup>5</sup> who have obtained formaldehyde and hydrogen peroxide

<sup>1</sup> Englemann, *Bot. Zeit.*, 1882, 40, 419

<sup>2</sup> Baeyer, *Ber.*, 1870, 3, 66

<sup>3</sup> Erlenmeyer, *Ber.*, 1877, 10, 634

<sup>4</sup> Bach, *Compt. rend.*, 1893, 116, 1145

<sup>5</sup> Usher and Priestley, *Proc. Roy. Soc.*, 1906, B, 77, 369



from aqueous carbon dioxide in presence of chlorophyll, formic acid, appearing as an intermediate substance. The same observers have shown<sup>1</sup> that this photosynthesis can be copied outside the green plant by the use of a suitable enzyme, but that for the formation of starch living non-chlorophyllous protoplasm is necessary. These observations are hardly in accord with that of Herzog,<sup>2</sup> to the effect that an extract of green leaves made like Buchner's extract of yeast has no power of carbon assimilation, but harmonise with the view that starch is not derived from photosynthetic sugar, but is a degradation product of protoplasm.

The proportion of carbon dioxide now present in the atmosphere is very nearly 3 parts in 10,000 by volume, or 0.03 per cent.

In the following table are included a few of the more important and recent determinations of the amount of carbon dioxide in the atmosphere.

Authority	Locality	Observation Parts of carbon dioxide by volume in 10,000 parts of air
J. Reiset, <i>Compt. rend.</i> , 1879, 88, 1007	Near Dieppe	2.912 (mean of 92 determinations)
A. Petermann and J. Graftman, <i>Chem. Zentr.</i> , 1892, ii, 201	Country air, Belgium	2.944 (mean)
Ditto	In town of Gembloux, Belgium	3.70 (mean)
W. C. Williams, <i>Ber.</i> , 1897, 30, 1450	Sheffield	3.9 (mean of numerous determinations in centre of city)
Ditto	One and a half mile west from centre of Sheffield	3.27 (mean)
M. de Thury, <i>Compt. rend.</i> , 1899, 129, 315	Mount Blanc altitude 1080 m	2.62
	altitude 3050 m	2.69
Letts and Blake, <i>Sci. Proc. Roy. Dub. Soc.</i> , 1900, 9, part ii, pp. 107-270	Belfast	2.91 (mean of 16 determinations)
H. T. Brown and E. F. Fycombe, <i>Proc. Roy. Soc.</i> , 1905, B, 76, 118	Kew	2.43-3.60 (minimum and maximum of numerous determinations during 1898 to 1901)

The total amount of carbon dioxide in the air is estimated at 2.2 billion ( $2.2 \times 10^{12}$ ) tons, and corresponds to the presence of 600,000 million tons of carbon.<sup>3</sup>

The sources of atmospheric carbon dioxide are respiration of man<sup>4</sup> and animals, and to a less degree of plants; combustion,<sup>5</sup> fermentation, and putrefaction of carbonaceous substances, frequently subterranean.

<sup>1</sup> Usher and Priestley, *Proc. Roy. Soc.*, 1906, B, 78, 318.

<sup>2</sup> Herzog, *Zeitsch. physiol. Chem.*, 1902, 35, 459.

<sup>3</sup> Krogh, *Meddelelser om Groenland*, 1904, 26, 419.

<sup>4</sup> It has been calculated that the human race exhales about one million tons of carbon dioxide into the air daily.

<sup>5</sup> The world's consumption of coal in 1913 was approximately 1200 million tons, and of this quantity the United Kingdom contributed 287.4 million tons, or approximately one-fourth.

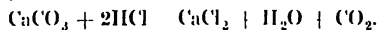
The soil is constantly evolving carbon dioxide; part of this is undoubtedly of volcanic origin, and part results from chemical change taking place nearer the surface of the soil. For example, small worms exhale as much carbon dioxide as human beings, weight for weight, and in view of the vast numbers of these and other lowly forms of life inhabiting the soil, it is easy to understand that the quantity of carbon dioxide evolved is considerable.<sup>1</sup>

Other sources of carbon dioxide are mineral springs, volcanic vents and fissures, and the calcination of carbonates, e.g. lime-burning. It was estimated by Boussingault in 1814 that Cotopaxi emitted more carbon dioxide annually than was produced by combustion and respiration in the city of Paris.

The accumulation in the atmosphere of the carbon dioxide derived from these various sources is prevented by the process of carbon-assimilation carried out in sunlight by green plants, and by the atmospheric weathering of siliceous rocks, which still continues. The relative magnitude of these two processes is not known, nor is it known how much carbon dioxide is annually removed from the air by their means, though T. C. Chamberlin<sup>2</sup> estimates this amount to be  $1.62 \times 10^9$  tons. Neither is it known whether the proportion of carbon dioxide in the air is now quite stationary, or whether it is very slowly increasing or diminishing. It may be supposed, however, that with the advance in human population and civilisation, and the accompanying depletion of forests, the proportion of carbon dioxide must be slowly increasing.

It has been shown by Arrhenius<sup>3</sup> that, owing to the power of absorbing terrestrial radiations possessed by carbon dioxide, an increase in the proportion of this gas in the atmosphere would increase the mean temperature of the latter. Thus Arrhenius calculates that if the quantity of carbon dioxide in the air were increased threefold the mean temperature of the Arctic regions would rise  $8^{\circ}$ – $9^{\circ}$  C., and that glacial periods may be accounted for by a loss of atmospheric carbon dioxide. Moreover, according to Høgbom,<sup>4</sup> it is the intermittent volcanic activity of the globe that disturbs the otherwise balanced proportion of carbon dioxide in the air; hence it would follow that varying volcanic activity is the determining cause of varying secular climate. This theory has not, however, found general acceptance, because it is known that variations in the amount of atmospheric aqueous vapour have a great, and probably preponderating, influence on terrestrial radiation.

**Preparation of Carbon Dioxide.** Carbon dioxide is generally prepared in the laboratory by the action of some what diluted hydrochloric acid on marble:



The appearance of the gas is preceded by the liberation of carbonic acid,  $\text{H}_2\text{CO}_3$ , which, being unstable, decomposes almost completely into water and carbon dioxide. The evolved gas, which contains traces of hydrochloric acid, may be purified by passing it through sodium hydrogen carbonate solution, or it may be collected over water instead of by the more usual method of upward displacement of air.

Dilute sulphuric acid cannot be employed in place of hydrochloric

<sup>1</sup> Friend, *Science Progress*, 1912, 6, 393.

<sup>2</sup> Chamberlin, *J. Geology*, 1899, 7, 682.

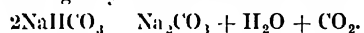
<sup>3</sup> Arrhenius, *Phil. Mag.*, 1896, [iv], 41, 237; *Ann. Physik.*, 1901, [iv], 4, 690.

<sup>4</sup> Høgbom, *Stensk. Kemisk Tidsskrift*, 1891, 6, 196; *Chem. Zentral.*, 1897, 1, 472.

acid because the marble quickly becomes encrusted with almost insoluble calcium sulphate which stops the action; if, however, concentrated sulphuric acid, containing only a very little water, is used, the evolution of gas continues because an acid sulphate of calcium is formed which remains in solution.

If sodium carbonate is employed as the source of carbon dioxide the evolution of the gas is vigorous, whether dilute hydrochloric or sulphuric acid is employed.

Sodium hydrogen carbonate is a convenient source of carbon dioxide, which it evolves when gently heated in the solid state or in solution:



Normal sodium carbonate is not decomposed by heat until a very high temperature is reached; calcium carbonate, being the salt of a less powerful base, begins to yield its carbon dioxide at about  $550^\circ\text{C}$ ; magnesium carbonate, in the form of the mineral magnesite, gives off carbon dioxide when gently ignited, and is therefore sometimes employed as a source of the gas.

Carbon dioxide may also be prepared by the combustion of charcoal or coke, and purified from the atmospheric nitrogen with which it will be mixed, by causing it to combine with an alkali carbonate, whence it is again set free by the action of acids.

**Physical Properties of Carbon Dioxide.**—Pure carbon dioxide is a colourless and odourless gas with a sharp taste. It is about one and a half times as heavy as air, and on this account accumulates in valleys, wells, and other low-lying spots. Thus the Poison Valley of Java is so named because carbon dioxide, issuing from fissures in the earth, remains in the valley, and may suffocate an unwary traveller; and the Grotto of Dogs, near Naples, similarly contains air richly laden with carbon dioxide to the depth of two or three feet, so that dogs or other small animals entering the Grotto are compelled to breathe the gas, whilst a man, walking with his head above the gas, is safe. The heaviness of carbon dioxide may be illustrated by pouring, lading, or siphoning the gas from one vessel to another, its presence being shown by the extinction of a taper. The density of the gas at  $0^\circ\text{C}$  and 760 mm (air = 1) is 1.52009 (Lord Rayleigh<sup>1</sup>) or 1.52894 (Leduc<sup>2</sup>), whilst the value calculated from the molecular weight is 1.5201. One litre of carbon dioxide at  $0^\circ\text{C}$  and 760 mm. weighs 1.9678 grams.<sup>3</sup>

The coefficient of thermal expansion of the gas at constant pressure has been determined by Chappuis<sup>4</sup> to be as follows:

Pressure	0–20° C	0–40° C	0–100° C.
At 518 mm.	0.0037128	0.0037100	0.0037073
.. 998 ..	0.0037602	0.0037536	0.0037410
.. 1377 ..	0.0037972	0.0037906	0.0037703

<sup>1</sup> Rayleigh, *Proc. Roy. Soc.*, 1897, 62, 204.

<sup>2</sup> Leduc, *Compt. rend.*, 1898, 126, 413.

<sup>3</sup> Dietrich, *Zeitsch. anal. Chem.*, 1864, 4, 142, see also Parr, *J. Amer. Chem. Soc.* 1909, 31, 237.

<sup>4</sup> Chappuis, *Trav. et Mém. du Bureau intern. des Poids et Mes.*, 1903, 13, 199.

**Compressibility.**—As will be shown below, carbon dioxide is an easily condensable gas; consequently when it is compressed it departs considerably from Boyle's law. The compressibility at various temperatures has been measured by Regnault,<sup>1</sup> Roth,<sup>2</sup> and Amagat.<sup>3</sup> The results of Amagat are given in the following table, which shows the values of  $pv$  when  $p$  is at 0° C. and 1 atm = 1.

Atm	0°	10°	20°	30°	40°	60°	80°	100	137°	198°	258°
50	0.105	0.114	0.680	0.775	0.850	0.964	1.096	1.206	1.380	—	—
100	0.202	0.213	0.229	0.255	0.309	0.661	0.873	1.030	1.259	1.582	1.847
150	0.295	0.309	0.326	0.346	0.377	0.485	0.681	0.878	1.159	1.530	1.818
200	0.385	0.401	0.419	0.440	0.468	0.543	0.660	0.815	1.096	1.496	1.804
300	0.559	0.578	0.599	0.623	0.649	0.710	0.790	0.890	1.108	1.493	1.820
400	0.728	0.748	0.771	0.795	0.823	0.884	0.956	1.039	1.218	1.563	1.883
500	0.891	0.913	0.938	0.963	0.990	1.051	1.121	1.201	1.362	1.678	—
700	1.206	1.232	1.259	1.289	1.319	1.383	1.454	1.529	1.676	1.956	—
1000	1.656	1.685	1.716	1.748	1.780	1.848	1.921	1.999	—	—	—

It will be seen from these figures that values of  $pv$  at a given temperature fall to a minimum as the pressure increases and then rise again; or the compressibility reaches a maximum at an intermediate pressure and then diminishes again. The following table shows the pressures at which  $pv$  reaches a minimum value at different temperatures.

Temperature °C	Pressure Atm.	Temperature °C	Pressure Atm.
0	35	70	162
10	45	80	179
20	57	90	196
30	76	100	211
40	101	137	247
50	121	198	255
60	143	258	218

The above phenomena are closely connected with those of the critical state investigated by Andrews,<sup>4</sup> who showed that above 31.1° C., which is called the *critical temperature*, no sensible liquefaction of carbon dioxide takes place, whatever the pressure; whilst below that temperature any isothermal, *i.e.* a curve showing the connection between volume and pressure at a particular temperature, consists of three parts representing: (i) compression of gas, (ii) liquefaction, (iii) compression of liquid. This is illustrated in Fig. 2, p. 118.

<sup>1</sup> Regnault, *Mém. de l'Acad.*, 1847, 26, 229

<sup>2</sup> Roth, *Wied. Annalen*, 1880, 11, 1

<sup>3</sup> Amagat, *Ann. Chim. Phys.*, 1881, [v], 22, 353, 1893, [vi], 29, 68, 508, *Compt. rend.*, 1890, 111, 871

<sup>4</sup> Andrews, *Phil. Trans.*, 1869, 159, 575; see also Knott, *Proc. Roy. Soc. Edin.*, 1900, 30, 1.

An examination of Amagat's results in the light of these considerations is instructive. The compressibility of carbon dioxide at  $0^{\circ}\text{C}$ . from 50 to 1000 atmospheres relates entirely to the liquid, and the same applies to the compressibility at  $10^{\circ}\text{C}$ . Carbon dioxide at  $20^{\circ}\text{C}$ . becomes liquid at about 57 atm., consequently the first value for  $pv$  in the third column of the table relates to gaseous carbon dioxide, and the

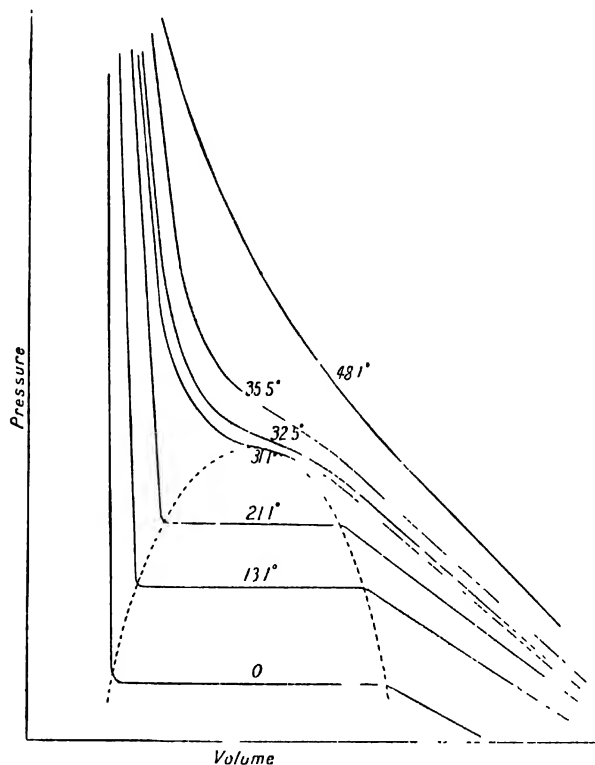


FIG. 2 — Isothermals of carbon dioxide, illustrating the critical phenomena

remaining values to the liquid; and the same is true for the values of  $pv$  at  $30^{\circ}\text{C}$ ., which lies just below the critical temperature. All the other values for  $pv$  in the table relate only to gaseous carbon dioxide.

These relationships appear clearly from the diagram in which isothermals are drawn, with pressures in atmospheres as abscissae and the values of  $pv$  as ordinates (Fig. 3). If carbon dioxide obeyed Boyle's law these isothermals would be horizontal straight lines. Thus the increasing departure of this substance from the condition of an ideal gas with lowering of temperature is illustrated, as well as the continuity of the gaseous and liquid states, which is especially shown

by the parallel lines to the right of the diagram, the last four of which pertain to liquid and the rest to gas. The vertical portions of the curve below  $30^{\circ}\text{C}$  represent the progress of liquefaction, and so far correspond to the horizontal portions of the curves in the previous figure.

**Liquid Carbon Dioxide.** Carbon dioxide was first liquefied by Faraday, in 1823, at a little below  $0^{\circ}\text{C}$ . under a pressure of 36 atm.

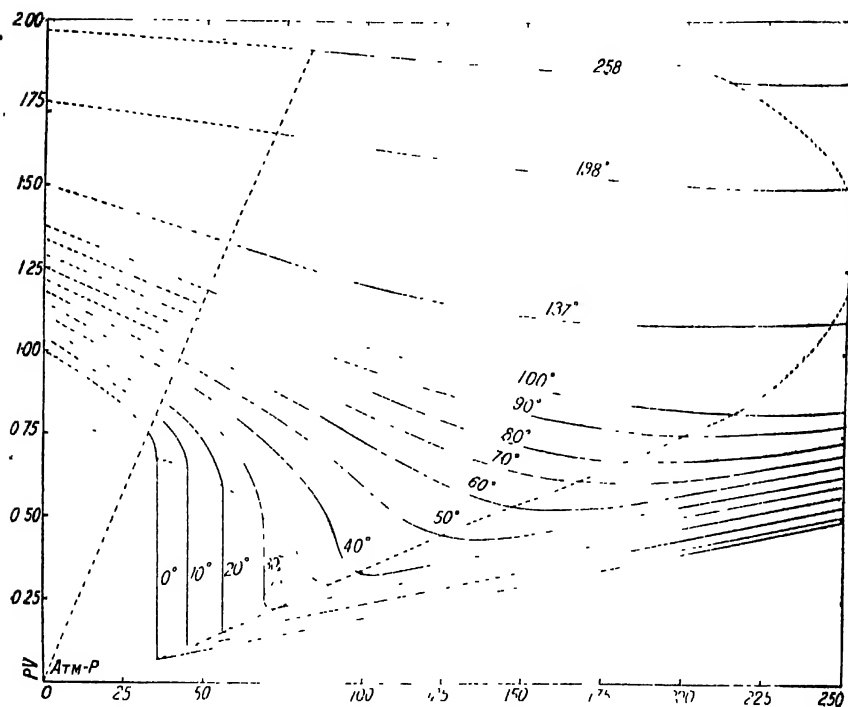


FIG. 3 — Isothermals of carbon dioxide showing the deviation of this gas from Boyle's law (Amagat)

(If  $pv = \text{constant}$ , the isothermal is a horizontal straight line.)  
See also vol. 1 (this series), p. 29

Faraday's apparatus was simple. Sulphuric acid acted on ammonium carbonate in one limb of a scaled, bent tube, and the gas was liquefied under its own pressure in the other limb, which was immersed in a freezing mixture.

The same principle was employed by Thilorier<sup>1</sup> on a larger scale, in 1839, the apparatus being made of cast-iron. Mateska and Donny improved on Thilorier's apparatus, with which fatal accidents had occurred, by employing two lead cylinders surrounded by copper and

<sup>1</sup> Thilorier, *Annalen*, 1839, 30, 122

connected by a narrow tube. The carbon dioxide was produced and liquefied in the generator, and then distilled into the receiver.

Natterer<sup>1</sup> and Bianchi compressed carbon dioxide by means of powerful pumps, so that it was liquefied in wrought-iron pear-shaped vessels. A similar method is still employed, cylinders of mild steel being substituted for wrought-iron vessels. Carbon dioxide derived from fermentation or from mineral springs is similarly compressed. Liquid carbon dioxide is employed as a refrigerator, for producing high pressures, and in the manufacture of mineral waters.

The vapour pressures of the liquid at different temperatures have been measured by Faraday<sup>2</sup> (1845), Regnault<sup>3</sup> (1862), Cailletet<sup>4</sup> (1878), Amagat<sup>5</sup> (1892), Villard<sup>6</sup> (1897), Kuenen and Robson<sup>7</sup> (1902), and Onnes and Weber<sup>8</sup> (1913). Zeleny and Smith<sup>9</sup> have obtained the following values for the vapour pressures of liquid carbon dioxide:

LIQUID CARBON DIOXIDE

Temperature °C	Pressure atm	Temperature °C	Pressure atm
— 65.5	3.30	— 40	9.88
— 60	4.35	— 30	11.31
— 56.1 (triple point)	5.11	— 20	19.52
— 50	6.73	— 10	25.83

The critical constants of carbon dioxide have been determined by different observers as follow:

Critical Temperature °C	Critical Pressure Atm.	Critical Volume	Critical Density	<i>a</i>	<i>b</i>	Observer
30.92	77.0	0.0066	—	0.00678	0.001807	Andrews <sup>10</sup>
31.35	72.9	—	0.464	0.00719	0.001912	Amagat <sup>11</sup>
31.9	77.0	—	—	0.00683	0.001813	Dewar <sup>12</sup>
31.00 ± 0.10	72.85 ± 0.10	—	—	—	—	Cardoso and Bell <sup>13</sup>

The constants *a* and *b* are those in van der Waals' equation:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

<sup>1</sup> Natterer, *J. prakt. Chem.*, 1845, 35, 169.

<sup>2</sup> Faraday, *Phil. Trans.*, 1823, 113, 160, 1845, 135, 4, 155.

<sup>3</sup> Regnault, *Mém. de l'Acad.*, 1862, 26, 335.

<sup>4</sup> Cailletet, *Arch. de Genève*, 1878, 66, 16.

<sup>5</sup> Amagat, *Compt. rend.*, 1891, 113, 446, 1892, 114, 1322.

<sup>6</sup> Villard, *Ann. Chim. Phys.*, 1897, [vi], 10, 387.

<sup>7</sup> Kuenen and Robson, *Phil. Mag.*, 1902, [vi], 3, 622.

<sup>8</sup> Onnes and Weber, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 215.

<sup>9</sup> Zeleny and Smith, *Physikal. Zeitsch.*, 1906, 7, 667.

<sup>10</sup> Andrews, *Phil. Trans.*, 1876, 166, 421.

<sup>11</sup> Amagat, *Compt. rend.*, 1892, 114, 1093.

<sup>12</sup> Dewar, *Phil. Mag.*, 1884, [v], 18, 210.

<sup>13</sup> Cardoso and Bell, *J. Chim. phys.*, 1912, 10, 497.

Liquid carbon dioxide is colourless; it is soluble in alcohol and ether, but does not mix with water; it dissolves various substances, among which are naphthalene and camphor, carbon disulphide, some hydrocarbons, boric acid, phosphorus pentachloride, arsenic and antimony tribromides, and yellow phosphorus, but iodine and bromine are only slightly soluble, and mercuric salts are insoluble in liquid carbon dioxide.<sup>1</sup>

The density of liquid carbon dioxide at various temperatures compared with that of the gas with which it is in equilibrium is shown by the following results obtained by Amagat <sup>2</sup>:

Temperature ° C	Liquid density	Gas density
0	0.914	0.096
10	0.856	0.133
20	0.766	0.190
30	0.598	0.331
30.5	0.574	0.356
31	0.536	0.392
31.35	0.464	0.461

It will be observed how these values approach each other towards the critical temperature at which, of course, they become identical.

**Solid Carbon Dioxide.** When a quantity of liquid carbon dioxide evaporates quickly the heat of vaporisation is withdrawn from the remaining liquid, which consequently freezes to a snowlike mass. This fact was observed by Thilorier; and an apparatus was devised by Natterer to be fixed to the valve of a cylinder of liquid carbon dioxide, so that when the valve is opened and the liquid is forced out by the pressure of the gas within the cylinder a quantity of carbon dioxide "snow" may be obtained. The apparatus consists of a cylindrical metal box, made in two parts which fit tightly together, and provided with a tube for the entrance of the liquid carbon dioxide, and pierced with holes beneath two hollow handles through which the gaseous carbon dioxide may escape. A piece of coarse canvas held over the valve of the cylinder whilst the liquid is escaping suffices, however, to collect some of the solid without the use of the box.

Solid carbon dioxide is crystalline, and has been obtained in cubes and octahedra<sup>3</sup>; when formed by the cooling of the liquid in bulk it is colourless and transparent like ice. It evaporates in the air without melting; this process is slow, however, because of the high heat of vaporisation.

The sublimation temperature at atmospheric pressure is  $-78.2^{\circ}\text{C}.$ ; and the vapour pressures at different temperatures are shown in the following table (Zeleny and Smith<sup>4</sup>).

<sup>1</sup> Buchner, *Zeitsch. physikal. Chem.*, 1906, 54, 665.

<sup>2</sup> Amagat, *Compt. rend.*, 1892, 114, 1093.

<sup>3</sup> Behnken, *Physical Review*, 1912, 35, 66.

<sup>4</sup> Zeleny and Smith, *Physikal. Zeitsch.*, 1906, 7, 667.



Temperature ° C	Pressure	Temperature ° C	Pressure
— 56.4 (triple point)	5.11 atm.	— 100	119 mm.
60	3.92 „	— 110	13 „
— 70	1.88 „	— 120	14 „
— 80	657 mm.	— 130	2.5 „
— 90	288 „	— 150 (Nernst)	0.05 „

The density of the compressed "snow"<sup>1</sup> is 1.2, whilst that of the "ice" is 1.56 at  $-79^{\circ}\text{C}$ . The "snow" may be handled without harm, but when pressed upon the skin for twenty seconds or more it produces blisters.

Solid carbon dioxide is now a commercial article, and is used therapeutically with more or less success in the treatment of the following diseases: warts, moles, erysipelas, eczema, lupus, and certain ulcers.<sup>2</sup> When employed in conjunction with certain liquids solid carbon dioxide is a valuable cooling agent. By passing a current of air at  $18^{\circ}\text{C}$ . through the following mixtures the following temperatures are obtained<sup>3</sup>: solid carbon dioxide with ethyl or methyl alcohol  $-85^{\circ}\text{C}$ ., with methyl chloride or acetaldehyde  $-90^{\circ}\text{C}$ ., with ethyl acetate  $-95^{\circ}\text{C}$ ., with acetone  $-98^{\circ}\text{C}$ .; whilst if the air is previously cooled to  $-80^{\circ}\text{C}$ . the temperature obtained with acetone is  $-110^{\circ}\text{C}$ . The theory of these phenomena from the standpoint of the phase rule has been worked out by Roozeboom.<sup>4</sup>

*Interrelationships of the Physical States of Carbon Dioxide.*—When a substance can exist in three physical states there is one condition under which the three states co-exist in equilibrium. If these states are represented on a pressure-temperature diagram (Fig. 4) this condition is expressed by a point called the triple point. The triple point for carbon dioxide is at  $-56.4^{\circ}\text{C}$ . and 5.1 atm. pressure; and it is represented in Fig. 4 at  $0_1$ .

$0_1A$ ,  $0_1B$ , and  $0_1C$  are the boundaries between liquid and vapour, solid and vapour, and solid and liquid respectively, and show the dependence of boiling-point, sublimation-point, and melting-point respectively upon pressure. The point  $0_4$  corresponds with  $-7.5^{\circ}\text{C}$ . and 2800 kg. per sq. cm. The upper part of the curve  $0_1C$ , i.e. the part  $0_4C$ , is broken to show a metastable condition, and the curves  $0_4D$  and  $0_4E$  are the boundaries of two forms of solid carbon dioxide discovered by Tammann.<sup>5</sup> Solid I can exist under the conditions represented by the curve  $0_4C$  as far as  $10.5^{\circ}\text{C}$ . and 4000 atm., but when the pressure is lowered it melts and passes into the more stable Solid II. The curve  $0_4E$ , along which Solid II and liquid can co-exist in equilibrium, has been traced as far as  $10.9^{\circ}\text{C}$ . and 3487 atm. When the pressure on Solid I above  $-7.5^{\circ}\text{C}$ . is increased the solid does not melt, but approaches the condition represented along the curve  $0_4D$ , in

<sup>1</sup> Landolt, *Ber.*, 1881, 17, 309

<sup>2</sup> See *Carbon Dioxide Snow*, by J. Hall-Edwards (Simpkin and Co., 1913)

<sup>3</sup> Moissan, *Compt. rend.*, 1901, 133, 768

<sup>4</sup> Roozeboom, *Helv. Chim. Acta*, 1904, ii, 340

<sup>5</sup> Tammann, *Wied. Annalen*, 1899, 68, 571, 629. *Chem. Zentr.*, 1912, ii, 598.

which the two solid forms are equally stable. This curve has been traced to  $15^{\circ}\text{C}$ . and 4000 atm.  $O_4$  is thus a triple point at which liquid carbon dioxide and its two solid forms co-exist in equilibrium, and by extending the curves  $AO_1$ ,  $BO_1$ ,  $DO_1$ , and  $EO_1$ , the imaginary triple points  $O_2$  and  $O_3$  come into view.

*Specific Heat* The specific heats of carbon dioxide and of other gases have been determined by the method of Regnault,<sup>1</sup> which consists

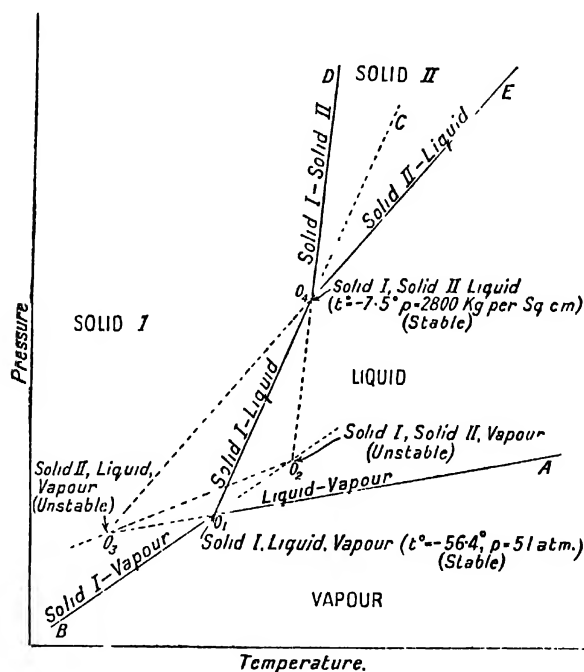


FIG. 4-- Equilibrium diagram of the physical states of carbon dioxide

in leading the heated gas through a spiral tube immersed in water and determining the amount of heat given up to the water; and by the method of Mallard and Le Châtelier,<sup>2</sup> in which, from the pressure developed in an enclosed space by explosion, the temperature attained is calculated, and thence from the known thermal data of the reaction the specific heat of the gas is derived.

Holborn and Austin,<sup>3</sup> employing the method of Regnault, estimated

<sup>1</sup> Regnault, *Mém. de l'Acad.*, 1862, 26, 1

<sup>2</sup> Mallard and Le Châtelier, *Compt. rend.*, 1881, 93, 962, 1011, 1076, 1887, 104, 1780; *Wied. Beibl.*, 1890, 14, 364. See also Berthelot and Vieille, *Ann. Chim. Phys.*, 1885, [vi], 4, 13; Saureau and Vieille, *Compt. rend.*, 1882, 95, 26; 1886, 102, 1054

<sup>3</sup> Holborn and Austin, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 175

the specific heat of carbon dioxide at constant pressure and different temperatures to be :

Temperature ° C	Specific Heat	Temperature ° C	Specific Heat
0	0.2028	400	0.2502
100	0.2161	600	0.2678
200	0.2285	800	0.2815

the general expression being :

$$C_p = 0.2028 + 0.0001384t - 0.00000005t^2.$$

Holborn and Henning<sup>1</sup> have more recently obtained a slightly different expression :

$$C_p = 0.2010 + 0.0000742t - 0.000000018t^2;$$

and Swann,<sup>2</sup> employing an electrical method, found the specific heat to be 0.20202 at 20° C and 0.22121 at 100° C.

Various thermal properties of carbon dioxide at low temperatures have been studied by Jenkin and Pye.<sup>3</sup>

The ratio of the specific heats at constant pressure and constant volume  $\left(\frac{C_p}{C_v}\right)$  has been estimated by numerous observers. Owing to the variation of the specific heat with pressure this ratio must correspondingly vary. The following values have been estimated by Amagat<sup>4</sup> at 50° C. and various pressures :

Atm		$C_p/C_v$
50	....	1.708
60	....	1.903
70	....	2.327

H. W. Moody<sup>5</sup> has found  $C_p, C_v$  at 20° C. and 760 mm. pressure to be 1.3003, whence  $C_p$  has been calculated to be 0.2008 under the same conditions.

The molecular heat of carbon dioxide at constant volume ( $C_v$ ) and the ratio  $\frac{C_p}{C_v} = \gamma$ , have been estimated by Crofts<sup>6</sup> by finding the temperature at which mixtures of this gas with electrolytic gas are fired by adiabatic compression; and the values of  $C_v$  have also been calculated from the formula

$$C_v = 6.6 + 0.0023t,$$

with the following results :

<sup>1</sup> Holborn and Henning, *Ann. Physik*, 1907, 23, 841.

<sup>2</sup> Swann, *Proc. Roy. Soc.*, 1909, A, 82, 117.

<sup>3</sup> Jenkin and Pye, *Phil. Trans.*, 1913, A, 213, 67.

<sup>4</sup> Amagat, *Compt. rend.*, 1895, 121, 862.

<sup>5</sup> Moody, *Physikal. Zeitsch.*, 1912, 13, 383.

<sup>6</sup> Crofts, *Trans. Chem. Soc.*, 1915, 107, 306.

Temperature Interval ° C	$\gamma$	Cr observed.	Cr calculated
15-532 . . .	1.254	7.815	7.823
15-545 . . .	1.253	7.847	7.853
15-557 . . .	1.252	7.878	7.881
15-570 . . .	1.251	7.909	7.911

The *heat of sublimation* of solid carbon dioxide was found by Behn<sup>1</sup> to be 142.4 calories per gram at  $-79^{\circ}\text{C}.$ , and the *heats of vapourisation* per gram of liquid carbon dioxide at different temperatures are, according to Cailliet and Mathias,<sup>2</sup> as follow

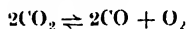
$t^{\circ}\text{C}$	Heat of Vapourisation
$-25$	72.23 calories
0	57.48 ..
$30.0$	11.60 ..
$30.82$	3.72 ..

The *heat of formation* of carbon dioxide is the same as the heat of combustion of carbon (*q<sub>r</sub>*), and therefore varies according to the kind of carbon which is burnt. Thomsen<sup>3</sup> gave the value 96,960 calories for  $(\text{C}, \text{O}_2)$  by the combustion of wood-charcoal, whilst the values obtained by Berthelot<sup>4</sup> were:

Diamond	Graphite	Amorphous Carbon
94,310 calories	94,810 calories	97,650 calories.

Through explosion in a calorific bomb, Berthelot<sup>5</sup> obtained the value 68,300 calories for the reaction  $(\text{C}, \text{O})$ .

**Decomposition of Carbon Dioxide.** Carbon-dioxide gas is very stable, and requires a high temperature for its decomposition. The thermal dissociation of this gas was first investigated by St. Claire-Deville,<sup>6</sup> who passed a rapid stream of it through a porcelain tube heated to about  $1300^{\circ}\text{C}.$ , and collected the issuing gas over potash solution. In this way the carbon dioxide was proved to be dissociated into carbon monoxide and oxygen to the extent of about 0.2 per cent. Le Chatelier<sup>7</sup> investigated the equilibrium represented by the equation



by igniting an explosive mixture of 2 volumes of carbon monoxide and 1 volume of oxygen which issued rapidly from a gas-burner, and causing the hottest part of the flame, whose temperature was estimated to be  $3000^{\circ}\text{C}.$ , to impinge upon a pierced silver tube through which a stream of water passed. The gases were thus drawn from the flame through the hole in the tube, and were collected and analysed. In

<sup>1</sup> Behn, *Ann. Physik*, 1900, **1**, 275

<sup>2</sup> Cailliet and Mathias, *J. Physique*, 1886, [n], **5**, 562, 1887, **6**, 411.

<sup>3</sup> Thomsen, *Thermochemische Untersuchungen*, 1882, n, 283

<sup>4</sup> Berthelot, *Compt. rend.*, 1889, **108**, 1141

<sup>5</sup> Berthelot, *Ann. Chim. Phys.*, 1878, [v], **13**, 11, 1881, [v], **23**, 177

<sup>6</sup> St. Claire-Deville, *Annales*, 1865, **134**, 121, 135, 94

<sup>7</sup> Le Chatelier, *Zetsch. physikal. Chem.*, 1868, **2**, 782

this way the dissociation of carbon dioxide was estimated to amount to 40 per cent. at 3000° C.

From this result, and assuming the gas pressure to be 1 atmosphere, Trevor and Kortwright<sup>1</sup> have calculated the percentages of dissociation of carbon dioxide at different temperatures and pressures to be as follow, the heat of dissociation  $Q_d$ , also being derived from the temperature.

Temp °C	0.001	0.01	0.1	1	10	100 Atm	$Q_d$
1000	0.11	0.05	0.024	0.011	0.005	0.0024	-62,662 cal.
1500	9.5	1.6	2.2	1.0	0.5	0.2	-56,125 ..
2000	57.7	31.7	18.3	9.0	4.3	2.0	-16,767 ..
2500	87.0	69.6	46.0	25.7	13.0	6.3	-31,610 ..
3000	93.9	83.4	62.7	40.0	21.6	10.8	-19,712 ..
3500	95.4	87.0	69.7	46.4	25.7	13.0	0
4000	95.1	86.4	66.6	45.0	21.9	12.6	+18,343 ..

It will be observed that the extent of dissociation reaches a maximum at about 3500° C at all pressures, and that at this temperature the heat of dissociation, which has been increasing from a negative value with rising temperature, passes through the zero-point and becomes positive. The figures in this table are calculated from a single experimental value, that of the dissociation at 3000° C under 1 atm., nevertheless the few other existing experimental values support them. The following results for the dissociation of carbon dioxide below 1300° C have more recently been obtained by Nernst and v. Wartenberg,<sup>2</sup> Langmuir,<sup>3</sup> and Loewenstem:<sup>4</sup>

Temperature °C	Per Cent (dissociation)	Observer
1027	0.00414	N. and W.
1122	0.0112	La.
1127	0.01 0.02	N. and W.
1170	0.025	La.
1205	0.029 0.035	N. and W.
1225	0.0471	La.
1277	0.04	Loc.
1292	0.064	La.

They agree accurately with values calculated from a formula.

The dissociation of carbon dioxide in the carbon monoxide-oxygen flame has been investigated by Haber and Rossignol, by the method

<sup>1</sup> Trevor and Kortwright, *Amer. Chem. J.*, 1894, 16, 618

<sup>2</sup> Nernst and v. Wartenberg, *Zeitsch. physikal. Chem.*, 1906, 56, 548

<sup>3</sup> Langmuir, *J. Amer. Chem. Soc.*, 1906, 28, 1,357

<sup>4</sup> Loewenstem, *Zeitsch. physikal. Chem.*, 1906, 54, 715.

of Deville, and these authors find that the value of the equilibrium constant  $K$  in the equation

$$K = \frac{[\text{CO}_2]}{[\text{CO}] \times [\text{O}_2]^{\frac{1}{2}}}$$

(where the brackets denote partial pressures) is about 4, which corresponds to a dissociation of about 37 per cent., the temperature of the flame being 2600–2670 °C.<sup>1</sup>

The dissociation of carbon dioxide at very high temperatures has been determined by Bjerrum,<sup>2</sup> by an explosive method, to be as follows:

T. ° abs. . . . .	1500°	2640°	2879°	2915	3116°
Dissociation per cent. . .	0.04	21.0	51.7	64.7	76.1

\* Carbon dioxide is decomposed into carbon monoxide and oxygen by means of electric sparks, a fact first observed by Henry<sup>3</sup>; whilst Buff and Hofmann<sup>4</sup> found that the decomposition is more rapid if steel electrodes are used, since these combine with the liberated oxygen. Even then, however, the decomposition is not complete,<sup>5</sup> but it rises to 65 per cent. when the pressure is reduced to 1 mm.<sup>6</sup> The silent electric discharge,<sup>7</sup> ultra-violet light,<sup>8</sup> and radium rays<sup>9</sup> also decompose carbon dioxide.

Carbon dioxide is decomposed by purely chemical means by heating sufficiently electropositive metals in the gas. Aluminium, for instance, reduces the gas according to the reaction:



and a piece of burning magnesium ribbon continues to burn in the gas with separation of carbon, thus



whilst potassium burns brilliantly in a stream of carbon dioxide with formation of carbonate and separation of carbon, thus:



*Absorption Spectrum of Carbon Dioxide.* Carbon dioxide is a colourless gas which shows no visible absorption spectrum: two absorption bands<sup>10</sup> occur, however, in the infra-red part of the spectrum, the maximum intensities of which correspond to the wave lengths 2.6 and 4.36  $\mu$ . The atmosphere shows these lines, and they are shown also by a flame in which carbon dioxide is being produced. Since they represent the absorption of radiant energy, they are the visible expression of the power possessed by carbon dioxide of hindering terrestrial radiation, which, according to Arrhenius, has had a great influence on climate.

*Solubility of Carbon Dioxide.* Water at atmospheric temperature dissolves about its own volume of carbon dioxide. The solubility

<sup>1</sup> Haber and Rosignol, *Zeitsch. physikal. Chem.*, 1909, 66, 181.

<sup>2</sup> Bjerrum, *Zeitsch. physikal. Chem.*, 1912, 79, 513, 537.

<sup>3</sup> Henry, *Phil. Trans.*, 1800.

<sup>4</sup> Buff and Hofmann, *Trans. Chem. Soc.*, 1860, 12, 293.

<sup>5</sup> Dixon and Lowe, *Trans. Chem. Soc.*, 1885, 47, 571.

<sup>6</sup> Collie, *Proc. Chem. Soc.*, 1902, 17, 168.

<sup>7</sup> Brodie, *Phil. Trans.*, 1874, 164, 83; Holt, *Trans. Chem. Soc.*, 1900, 95, 30.

<sup>8</sup> Chadwick, Ramsbottom, and Chapman, *Proc. Chem. Soc.*, 1900, 22, 23; Herche-finkel, *Compt. rend.*, 1909, 149, 395.

<sup>9</sup> Cameron and Ramsay, *Trans. Chem. Soc.*, 1908, 93, 967.

<sup>10</sup> Angstrom, *Wied. Annalen*, 1890, 39, 267; Paschen, *Wied. Annalen*, 1893, 50, 409, 1894, 51, 1, 40, 52, 209, 53, 334.

coefficient  $c$  was determined by Bunsen<sup>1</sup> at different temperatures with the following results:

Temperature °C.	0°	5°	10	15°	20°
$c$	1.7967	1.1197	1.1847	1.0020	0.9014

the general equation being:

$$c = 1.7967 - 0.07761t + 0.001642t^2.$$

The following values have been obtained more recently by Bohr and Bock<sup>2</sup> ( $c$  vol. per vol.;  $g$  gram per 100 grams):

Temp °C	$c$	$g$	Temp °C	$c$	$g$
0	1.713	0.3317	18	0.928	0.1789
1	1.616	0.3214	19	0.902	0.1736
2	1.584	0.3091	20	0.878	0.1689
3	1.527	0.2979	21	0.854	0.1641
4	1.473	0.2872	22	0.829	0.1591
5	1.424	0.2774	23	0.804	0.1541
6	1.377	0.2681	24	0.781	0.1494
7	1.331	0.2590	25	0.759	0.1459
8	1.282	0.2494	26	0.738	0.1407
9	1.237	0.2404	27	0.718	0.1367
10	1.194	0.2319	28	0.699	0.1328
11	1.154	0.2240	29	0.682	0.1293
12	1.117	0.2166	30	0.665	0.1259
13	1.083	0.2099	35	0.592	0.1106
14	1.050	0.2033	40	0.530	0.0974
15	1.019	0.1971	45	0.479	0.0862
16	0.985	0.1904	50	0.436	0.0762
17	0.956	0.1815	60	0.359	0.0577

At low pressures the solubility of carbon dioxide in water accords with Henry's law, but at high pressures solubility does not keep pace with pressure, so that the ratio  $\frac{S}{P}$  diminishes instead of remaining constant. The following results were obtained by Wroblewski<sup>3</sup>

P. (atm)	S at 0° C	$\frac{S}{P}$
1	1.797	1.797
5	8.65	1.730
10	16.03	1.603
15	21.95	1.463
20	26.65	1.332
25	30.55	1.222
30	33.74	1.124

<sup>1</sup> Bunsen, *Gasometrische Methoden*, 1857.

<sup>2</sup> Bohr and Bock, *Wied. Annalen*, 1891, 44, 318.

<sup>3</sup> Wroblewski, *Wied. Annalen*, 1883, 18, 290.

Sander<sup>1</sup> finds, however, that Henry's law is the more nearly followed the higher the temperature, and that at 100° C. the solubility of carbon dioxide in most solvents is proportional to the pressure.

When carbon dioxide has been dissolved in water under pressure—as, for instance, in the manufacture of mineral waters—the excess does not immediately leave the solution upon removal of the excess of pressure. The state of supersaturation is, however, disturbed by particles of dust or a rough surface.

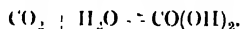
A crystalline hydrate,  $\text{CO}_2 \cdot 8\text{H}_2\text{O}$ , is formed from water at about 0° C. and carbon dioxide at 25 atm., which is permanent until the pressure is reduced to 12.7 atm. The hydrate may, however, be  $\text{CO}_2 \cdot 6\text{H}_2\text{O}$ .<sup>2</sup>

The solubility of carbon dioxide in alcohol is more than twice its solubility in water; it is given by the expression<sup>3</sup>

$$c = 4.3294 - 0.09126t + 0.001235t^2$$

This gas also dissolves in many other organic solvents in all of which it is distinctly more soluble than in water. The depression of the freezing-point of benzene and acetic acid by dissolved carbon dioxide shows that this substance possesses the normal molecular weight in these solutions.<sup>5</sup> The solubility of carbon dioxide in colloidal liquids and fine suspensions has been investigated by Findlay, Crighton, Shen, and Williams,<sup>6</sup> and the influence of non-electrolytes on the solubility of this gas in water by Usher.<sup>7</sup>

**Carbonic Acid.**—When carbon dioxide dissolves in water it produces a feeble acid which turns the colour of ordinary blue litmus a port-wine red<sup>8</sup> and discharges the crimson colour of phenolphthalein, but scarcely affects methyl orange. This acid is (meta) carbonic acid,  $\text{H}_2\text{CO}_3$ , formed by the hydroxylation of carbon dioxide, thus



When an aqueous solution of carbonic acid is boiled the acid is completely decomposed, with the escape of carbon dioxide, so that the original colour of an indicator, which had been changed by the carbonic acid, is restored.

The acidity of carbonic acid is due to its dissociation into the ions  $\text{H}^+$  and  $\text{HCO}_3^-$ , thus:



and the extent to which this reaction has taken place when equilibrium is reached is indicated by the electric conductivity of the solution. This conductivity was measured, first by Pfeiffer,<sup>9</sup> later by Knox,<sup>10</sup> and also by Walker and Cormack.<sup>11</sup>

<sup>1</sup> Sander, *Zeitsch. physikal. Chem.*, 1912, 78, 511.

<sup>2</sup> Wroblewski, *Bull. Acad. Sciences*, 1883, 18, 290; Hempel and Seidel, *Ber.*, 1898, 31, 2997.

<sup>3</sup> Villard, *Compt. rend.*, 1891, 119, 363; *Ann. Phys. Chem.*, 1897, [59], 11, 289.

<sup>4</sup> Henrich, *Zeitsch. physikal. Chem.*, 1892, 6, 435.

<sup>5</sup> Gaetli and Falcova, *Atti R. Accad. Lincei*, 1904, [5], 13, 1, 110.

<sup>6</sup> Findlay and Crighton, *Trans. Chem. Soc.*, 1910, 97, 536; Findlay and Shen, 1912, 101, 1459; Findlay and Williams, 1913, 103, 636; see also Findlay and King, *Trans. Chem. Soc.*, 1913, 103, 1170, 1914, 105, 1297; also Findlay and Howell, *Trans. Chem. Soc.*, 1915, 107, 282.

<sup>7</sup> Usher, *Trans. Chem. Soc.*, 1910, 97, 66.

<sup>8</sup> Water saturated with carbon dioxide should turn litmus the full acid colour. That it does not is probably due to the presence of chalky impurity in the litmus.

<sup>9</sup> Pfeiffer, *Ann. Phys. Chem.*, 1881, 23, 625.

<sup>10</sup> Knox, *Ann. Phys. Chem.*, 1895, 54, 44.

<sup>11</sup> Walker and Cormack, *Trans. Chem. Soc.*, 1900, 77, 8.



The following results were obtained by Walker and Cormack at a temperature of 18° C.:

CARBONIC ACID,  $\text{H}_2\text{CO}_3$ 

From Marble				From solid $\text{CO}_2$			
$c$	$\lambda_0$	$\gamma$	K	$c$	$\lambda_0$	$\gamma$	K
31.25	1.038	0.00309	0.00306	27.5	0.972	0.00289	0.00305
62.5	1.175	0.00139	309	55.0	1.368	0.00107	303
93.7	1.800	0.00536	308	82.5	1.679	0.00500	301
125.0	2.083	0.00620	309	110.0	1.930	0.00775	302
		Mean	0.00308			Mean	0.00301

where

$c$  volume in litres containing 1 gram molecule of  $\text{CO}_2$

$\lambda_0$  molecular conductivity determined by experiment

$\gamma$  proportion of acid dissociated

$\lambda = \frac{\lambda_0}{\gamma} = \frac{\lambda_\infty}{3.36}$  where 3.36 = molecular conductivity at infinite dilution

K dissociation constant

$$= \frac{\gamma^2}{(1-\gamma)c} \quad (\text{Ostwald's dilution law}).$$

The figures under  $\gamma$  convey no information as to the degree of hydroxylation of the carbon dioxide in solution<sup>1</sup>; that is as to what proportion has been converted into  $\text{H}_2\text{CO}_3$ , some of which is subsequently dissociated, and what proportion remains as  $\text{CO}_2$ ; they show, however, the ratio of the concentration of H ions to the possible concentration if all the carbon dioxide were present as dissociated carbonic acid.

Since the strength of an acid is indicated by the relative magnitude of its dissociation constant K it is useful to compare the relative strengths of carbonic and other acids.

In the table on the opposite page are given the dissociation constants of the more common weak inorganic acids, together with their percentage ionisation in decinormal and centinormal solutions, as calculated by the aid of Ostwald's dilution formula (*vide supra*). The values for hydrochloric acid are calculated direct from the conductivity at the above-mentioned concentrations and at infinite dilution. These figures are of practical utility. Thus, if equivalent quantities of acetic and carbonic acids compete for an equivalent of a base in decinormal solution, we are able to say that the base will be shared between the acids in the ratio 1.3 : 0.25, the acetic acid thus taking about five times as much of the base as the carbonic acid.

<sup>1</sup> This series, vol. 1, p. 222

<sup>2</sup> Walker, *Trans. Chem. Soc.*, 1903, 83, 182

Acid	Temp °C	K	100 γ	
			N 100 Solu	N 10 Solu
Hydrochloric, <sup>1</sup> Cl-H	18		97.1	92.6
Nitrous, <sup>2</sup> NO <sub>2</sub> -H	25	5 × 10 <sup>-11</sup>	20.0	5.0
Acetic, <sup>3</sup> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> -H	18	1.8 × 10 <sup>-5</sup>	1.2	1.30
Carbonic, <sup>4</sup> HCO <sub>3</sub> -H	18	3 × 10 <sup>-7</sup>	0.771	0.25
Carbamic, <sup>5</sup> HCO <sub>2</sub> -H	18	5 × 10 <sup>-4</sup>	29.0	9.5
Sulphydic, <sup>2</sup> HS-H	18	9 × 10 <sup>-8</sup>	0.12	0.13
Boric, <sup>1</sup> H <sub>2</sub> BO <sub>3</sub> -H	18	5.8 × 10 <sup>-10</sup>	0.012	0.013
Hydrocyanic, <sup>6</sup> CN-H	18	1.3 × 10 <sup>-9</sup>	0.036	0.011
Water, <sup>6</sup> HO-H	18	0.71 × 10 <sup>-11</sup>		--

The degree of ionisation of the second hydrogen atom of H<sub>2</sub>CO<sub>3</sub> has been estimated by several observers, the most reliable value<sup>7</sup> being:

$$K \frac{CO_3^{--} H}{HCO_3^-} = 6 \times 10^{-11}$$

The "true strength" of carbonic acid has been estimated by Thiel and Strohecker.<sup>8</sup> By the "true strength" is meant the degree of ionisation of the H<sub>2</sub>CO<sub>3</sub> actually formed rather than the ionisation with reference to CO<sub>2</sub> dissolved. It has been found that in a 0.00812-M solution of carbon dioxide at 1°C only 0.67 per cent is present as carbonic acid. The "true strength" of carbonic acid is therefore  $\frac{100}{0.67}$  times its strength found from conductivity measurements. Thus the true dissociation constant is  $5 \times 10^{-7}$  instead of  $3 \times 10^{-7}$ , and the acid is found to be twice as "strong" as formic acid. Such a conclusion might be anticipated, since carbonic acid is hydroxyformic acid.

**The Carbonates.** Carbon dioxide might be expected to undergo hydroxylation in two stages, producing respectively metacarbonic acid, CO(OH)<sub>2</sub>, and orthocarbonic acid, C(OH)<sub>4</sub>.

It has been shown, however, that even the former acid is unstable, and neither the latter acid nor its inorganic salts exist. Alkyl orthocarbonates are, however, known, e.g., ethyl orthocarbonate, C(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>.

<sup>1</sup> Noyes, *Caracque Publications*, No. 63, 1907, pp. 137, 262, *Zeitsch. physikal. Chem.*, 1910, 70, 337. See this series, vol. viii, p. 105.

<sup>2</sup> See this series, vol. i, p. 223.

<sup>3</sup> Kohlrausch and Holborn, *Zeitsch. physikal. Chem.*, 1894, 14, 321.

<sup>4</sup> Walker and Cormack, *Trans. Chem. Soc.*, 1900, 77, 5.

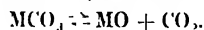
<sup>5</sup> Thiel and Strohecker, *vide infra*.

<sup>6</sup> Calculated from data given by Landen, *J. Chem. phys.*, 1907, 5, 571.

<sup>7</sup> Auerbach and Pick, *Arbeitsausd. Kaiserlich Gesundheitsamt*, 1912, 38, [ix], 562. See also "General Equations for the Neutralization of Dibasic Acids, and their Use to Calculate the Acidity of Dilute Carbonate Solutions," E. B. R. Prudden, *Proc. Roy. Soc.*, 1915, A, 91, 535.

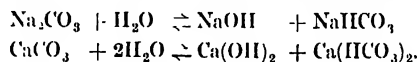
<sup>8</sup> Thiel and Strohecker, *Ber.*, 1914, 47, 915.

Carbonic acid,  $\text{H}_2\text{CO}_3$ , readily decomposes into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ,<sup>1</sup> and the carbonates tend to undergo a similar reversible reaction:

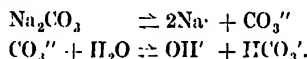


The stability of a carbonate depends on the strength of the base contained in it. Thus the alkali carbonates are scarcely decomposable at a white heat; the alkaline earth carbonates lose carbon dioxide at a red heat, barium carbonate being the most stable of the three; carbonates of magnesium, zinc, copper, etc., lose carbon dioxide even more readily, and are prone to form basic carbonates, the formation of the normal salt by precipitation requiring the presence of excess of carbonic acid. Metalloids such as tin and antimony, and extremely electronegative metals like gold and platinum, form no carbonates.

The carbonates of the alkali metals are readily soluble in water; other carbonates are very slightly soluble, or practically insoluble. So far as water can act on carbonates, it hydrolyses them into free base or basic salt and free carbonic acid or hydrogen salt. Thus sodium and calcium carbonates undergo the following reactions with water—the former considerably, the latter, owing to its small solubility, very slightly:



The former of these reactions has been carefully studied. It may be otherwise represented:



The extent of hydrolysis in aqueous solution is indicated by the amount of alkalinity developed, that is by the excess of  $\text{OH}^-$  over  $\text{H}^+$  ions in the solution. Such alkalinity cannot be estimated by titration because the disturbance of equilibrium by the addition of  $\text{H}^+$  ions is accompanied by further hydrolysis till equilibrium is restored.

The saponification of an ester, however, is a reaction which may be utilised, since neither  $\text{H}^+$  nor  $\text{OH}^-$  ions are thereby added to the solution, and the rate of such saponification is directly proportional to the concentration of  $\text{OH}^-$  ions. This method has been employed by Shields,<sup>1</sup> who found that the sodium carbonate in a  $\frac{N}{10}$  solution is hydrolysed at  $25^\circ$  to the extent of 3.17 per cent.

**Bicarbonates.**—Only the most electropositive metals form bicarbonates or hydrogen carbonates. The bicarbonates of the alkali metals, excepting lithium, are known in the solid state, and are less soluble in water than the corresponding carbonates. They show a progressive stability with increase in electropositiveness from sodium to cesium.<sup>2</sup> The bicarbonates of lithium, calcium, strontium, barium, and ferrous iron exist only in solution, and are more soluble in water than the normal carbonates.

**Double or Complex Carbonates.**—Salts of the type  $\text{MKH}(\text{CO}_3)_2$ , where M is cobalt, nickel, or magnesium, were obtained by Deville.<sup>3</sup>

<sup>1</sup> Shields, *Zeitsch. physikal Chem.*, 1893, 12, 167.

<sup>2</sup> Caven and Sand, *Trans. Chem. Soc.*, 1911, 99, 1359; 1914, 105, 2752.

<sup>3</sup> Deville, *Ann. Chim. Phys.*, 1851, [iii], 33, 75.

and were converted into salts of the type  $MK_2(CO_3)_2$  by heating their solutions. Other complex salts of the same type, whose constitution is probably  $KCO_3 \cdot MCO_3 \cdot K$ , were prepared by Reynolds.<sup>1</sup>

The metallic carbonates, bicarbonates, and complex carbonates will be dealt with under the individual metals.

**Physiological Action of Carbon Dioxide.** Respiration in man is directly related to the proportion of carbon dioxide in the air of the lung alveoli. Breathing regulates the fluctuations due to varying carbon dioxide production within the body, or varying carbon dioxide pressures in the inspired air; and there is maintained during rest a fixed partial pressure of about 5.6 per cent, or 40 mm. within the lungs. A rise of about 0.22 per cent, or 1.6 mm. in this pressure increases the rate of breathing by 100 per cent., and a corresponding diminution of alveolar carbon dioxide causes apnoea<sup>2</sup> (cessation of natural breathing).

"When the alveolar carbon dioxide reaches about 8 per cent, dizziness and loss of memory, etc., begin. With higher percentages there is loss of consciousness, but no immediate danger till the percentage exceeds 20 or 30. Recovery is rapid and complete."<sup>3</sup>

The action of carbon dioxide within the blood depends upon the formation of carbonic acid, and the consequent hydron concentration reached by this acid. Apart from the fluctuations caused by varying carbon dioxide pressure, this concentration is regulated with exquisite exactitude, chiefly by the kidneys.<sup>2</sup>

As regards the relation between oxygen and carbon dioxide in the blood, oxygenation of the blood in the lungs helps to drive out carbon dioxide and increases by about 50 per cent. the amount of carbon dioxide given off at each round of the circulation, whilst the de-oxygenation of the blood in the tissues helps the absorption of carbon dioxide and diminishes by about 40 per cent. the rise of carbon dioxide pressure and of hydron concentration in the venous blood. Thence it follows that the giving off of carbon dioxide by the lungs is to a large extent consequent on the taking up of oxygen.<sup>1</sup>

**Detection and Estimation of Carbon Dioxide.** Carbon dioxide is detected by its action on lime-water, which it turns milky owing to the precipitation of calcium carbonate. Barley water may be used instead of lime-water. Owing to its formation of a feeble acid with water, carbon dioxide turns the colour of blue litmus solution,<sup>4</sup> or moistened litmus paper, to a port-wine red. On boiling the solution, or drying the paper, the blue colour returns, because of the decomposition of the carbonic acid.

Carbon dioxide may be estimated: (i) gasometrically, (ii) gravimetrically, (iii) titrimetrically.

(i) The proportion of carbon dioxide in a gaseous mixture is estimated by the diminution of volume which takes place when a measured volume of the gas is shaken with concentrated potash or soda solution, or allowed to stand in contact with the moistened solid alkali. All other gases which combine with alkali, such as sulphur dioxide, nitrogen peroxide, and chlorine, must, of course, be absent from the mixture.

<sup>1</sup> Reynolds, *Trans. Chem. Soc.*, 1898, 73, 262.

<sup>2</sup> Campbell, Douglas, Haldane, and Hobson, *J. Physiol.*, 1913, 46, 301.

<sup>3</sup> Private communication from Dr. J. S. Haldane.

<sup>4</sup> Christiansen, Douglas, and Haldane, *J. Physiol.*, 1914, 48, 244.

<sup>5</sup> See note \* on page 129.

The estimation is carried out by the use of Hempel's or other apparatus<sup>1</sup> for gas analysis.

(ii) Carbon dioxide is estimated gravimetrically (a) by the loss of weight consequent upon the evolution of the gas from a carbonate, (b) by the direct weighing of such evolved gas after its absorption by alkali, (c) by converting the evolved carbon dioxide into barium carbonate, which is weighed.

(a) The amount of carbon dioxide in a carbonate or mixture of carbonates may occasionally be estimated by ignition. For instance, the proportion of chalk in a mixture of this substance with quicklime might be so estimated; likewise the proportion of sodium bicarbonate mixed with carbonate, by reckoning the loss on ignition as carbonic acid ( $\text{H}_2\text{CO}_3$ ). This method, however, is of limited application unless means are taken to retain the water which is frequently present in basic carbonates, and would also be evolved on ignition. More often the carbon dioxide is evolved by the action of acid upon the carbonate contained in a specially constructed apparatus such as that of Geissler or Schotter. When the action of the acid is completed the resulting solution is warmed, and air is then aspirated through the apparatus to displace the remaining carbon dioxide, loss of water-vapour being prevented by causing the escaping air to bubble through concentrated sulphuric acid. The loss in weight of the whole apparatus is the weight of the carbon dioxide expelled.

(b) A more accurate, and indeed the most satisfactory, way of estimating carbon dioxide is to cause the evolved gas to pass through drying tubes containing sulphuric acid or calcium chloride, and then into strong potash solution contained in "potash bulbs," to which is attached a small calcium chloride tube to retain water-vapour carried forward by the passing gas. This method is employed for the estimation of carbonates, which are decomposed by acid; and also for determining the carbon and hydrogen present in an organic compound. For this purpose the compound is burnt in a stream of air or oxygen in a combustion tube with the aid of copper oxide, the resulting water-vapour being absorbed in calcium chloride and the carbon dioxide in potash. Soda-lime contained in a U-tube together with calcium chloride, to absorb water-vapour from the soda-lime, may be employed in place of potash.

(c) The amount of carbon dioxide in a gaseous mixture or in aqueous solution can be estimated by causing it to react with ammoniacal barium chloride solution, and then carefully collecting, washing with  $\text{CO}_2$ -free water, drying, and weighing the resulting barium carbonate.

(iii) The carbon dioxide in a gaseous mixture—as, for instance, in air—is determined by titration (Pettenkofer). A measured volume of standard baryta water is added in excess to, and shaken with, a known volume of the gas in a large bottle, and the remaining baryta is then titrated with standard acid in presence of phenolphthalein. From the amount of baryta carbonated the amount of carbon dioxide in the gas is calculated.

Alkali carbonates in solution are also estimated by well-known volumetric methods.

It has been shown by Warburg<sup>1</sup> that a hot solution of barium hydroxide absorbs carbon dioxide far more rapidly than a cold solution.

<sup>1</sup> Warburg, *Zeitsch. physiol. Chem.*, 1909, 61, 261.

and that by this means small quantities such as 0.001 gram may be estimated.

Davies and McLellan<sup>1</sup> have described a modification of the Lunge-Zeekendorf method of estimating carbon dioxide in the air, depending upon the number of strokes of a pump drawing 50 c.c. of air per stroke through standard bartha water containing phenolphthalein, which are necessary to decolourise the solution.

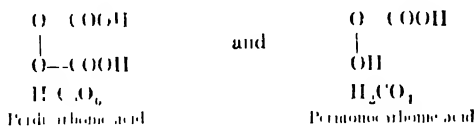
### PERCARBONIC ACID AND ITS SALTS

Per-acids are derivatives of hydrogen peroxide, and, like that substance, contain a chain of two oxygen atoms. This chain may, however, occupy an internal or an external position with reference to the rest of the molecule; the difference is illustrated by perdisulphuric and permonosulphuric acids, in the former of which the oxygen chain is internal, in the latter necessarily external, one only of the two hydrogen atoms of  $H_2O_2$  being replaced by an acidic group, thus:



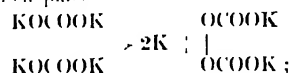
It may be remarked that the former is prepared electrolytically and results from the union of two  $-OSO_2OH$  groups at the anode, whilst the latter is obtained by chemical means.

Two percarbonic acids may similarly be supposed to exist:



The first formula may be applied to the percarbonate obtained by electrolysis<sup>2</sup>; a percarbonate or collateral constitution results from the union of a superoxide and carbon dioxide, to which the second formula may be applied. It may be noted also that an isomer with the former acid is possible, viz.  $O-C(O)OOH$ .

Potassium percarbonate,  $K_2C_2O_6$ , was first prepared by Constam and von Hansen,<sup>3</sup> in 1897-8, by the electrolysis of a concentrated solution of potassium carbonate at  $-10^\circ C.$  to  $-15^\circ C.$ , and by subsequent treatment was obtained nearly pure. The following reaction appears to have taken place:



and the product was a bluish-white, amorphous powder, stable at atmospheric temperature in the dry state, but decomposed by cold water with the evolution of oxygen, which comes off in a continuous

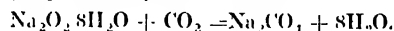
<sup>1</sup> Davies and McLellan, *J. Soc. Chem. Ind.*, 1900, 28, 232.

<sup>2</sup> Bach, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 373; *Chem. Zentr.*, 1897, [u], 828.

<sup>3</sup> Constam and von Hansen, *Zeitsch. Elektrochem.*, 1897-8, 3, 137, 145.

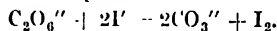
stream at 45° C. It is important to note that sodium percarbonate could not be prepared by electrolysis because the carbonate does not yield a sufficiently strong solution with water.

Alternative methods, however, of preparing sodium percarbonate are by the interaction of sodium carbonate and hydrogen peroxide, or of sodium peroxide and carbon dioxide. Tanatar<sup>1</sup> employed the former method, and isolated two salts having the composition  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$  and  $2\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , but was in doubt whether these were true percarbonates or compounds of sodium carbonate with hydrogen peroxide. By the interaction of solid hydrated sodium peroxide and solid carbon dioxide Bauer<sup>2</sup> obtained a percarbonate of the composition  $\text{Na}_2\text{CO}_3$ , according to the reaction:



By means of hydrogen peroxide Kasanezky<sup>3</sup> has prepared the potassium salt  $2\text{K}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$  or  $2[(\text{K} \cdot \text{O} \cdot \text{O})_2\text{CO}] \cdot 5\text{H}_2\text{O}$  and the ammonium salt  $\text{NH}_4\text{O} \cdot \text{O} \cdot \text{CO} \cdot \text{O} \cdot \text{NH}_4 \cdot 2\text{H}_2\text{O}$ ; whilst Wollfenstein and Peltner<sup>4</sup> by the interaction of sodium peroxide and carbon dioxide, obtained not only the salt  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , previously prepared by Tanatar, but "sodium dioxide dicarbonate"  $\text{Na}_2\text{C}_2\text{O}_6$ ; and in other ways "sodium trioxide dicarbonate"  $\text{NaHCO}_3$  or  $\text{Na}_2\text{C}_2\text{O}_7$ ; another salt isomeric with this, and "sodium trioxide carbonate"  $\text{Na}_2\text{C}_3\text{O}_9$ . Subsequently Peltner<sup>5</sup> obtained the following rubidium salts from the carbonate and hydrogen peroxide:  $\text{Rb}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Rb}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ , and  $2\text{Rb}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$ ; and shortly afterwards Riesenfeld and Reinhold,<sup>6</sup> after preparing pure potassium percarbonate,  $\text{K}_2\text{C}_2\text{O}_6$ , by electrolysis, attacked the problem which was pressing in view of the supposed existence of all the above salts, as to whether a true percarbonate could be distinguished from a compound of a carbonate with hydrogen peroxide.

These authors found that the electrolytic percarbonate immediately liberates iodine from a cold solution of potassium iodide without loss of oxygen according to the equation:



This reaction is not due to the previous liberation of hydrogen peroxide, since this substance reacts but slowly with potassium iodide. Tanatar's percarbonate, however, prepared from carbonate and hydrogen peroxide, liberates oxygen when mixed with neutral potassium iodide solution, and was therefore supposed to be a compound of carbonate and hydrogen peroxide. At the same time doubt was thrown upon the nature of Wollfenstein and Peltner's percarbonates. Thereupon ensued a controversy between Riesenfeld<sup>7</sup> on the one hand and Tanatar<sup>8</sup> and Wollfenstein<sup>9</sup> on the other; at the end of which Riesenfeld and Mau<sup>10</sup> maintained that a true percarbonate can be distinguished from

<sup>1</sup> Tanatar, *Ber.*, 1899, 32, 1514, *J. Russ Phys. Chem. Soc.*, 1902, 34, 952.

<sup>2</sup> Bauer, *Chem. Zentr.*, 1903, [ii], 1034.

<sup>3</sup> Kasanezky, *J. Russ Phys. Chem. Soc.*, 1903, 35, 57, 1902, 34, 202.

<sup>4</sup> Wollfenstein and Peltner, *Ber.*, 1908, 41, 280.

<sup>5</sup> Peltner, *Ber.*, 1909, 42, 1777.

<sup>6</sup> Riesenfeld and Reinhold, *Ber.*, 1909, 42, 4377.

<sup>7</sup> Riesenfeld, *Ber.*, 1910, 43, 566, 2594.

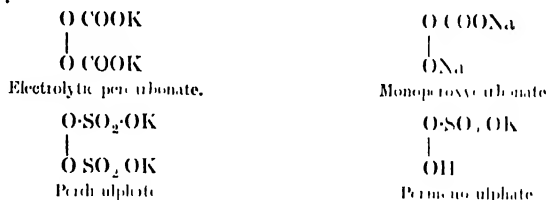
<sup>8</sup> Tanatar, *Ber.*, 1910, 43, 127, 2149.

<sup>9</sup> Wollfenstein, *Ber.*, 1910, 43, 639.

<sup>10</sup> Riesenfeld and Mau, *Ber.*, 1911, 44, 3589, 3595.

carbonates containing hydrogen peroxide of crystallisation by the quantitative liberation of iodine from neutral potassium iodide solution, and subsequently classified carbonates containing peroxidic oxygen in the following way: (1) carbonates containing hydrogen peroxide of crystallisation, *e.g.*  $2\text{Na}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}_2$ ; (2) monoperoxy-carbonates, *e.g.*  $\text{Na}_2\text{C}_2\text{O}_4$ ; (3) percarbonates (monoperoxy-dicarbonates), *e.g.*  $\text{Na}_2\text{C}_2\text{O}_6$ . The latter salt, prepared from sodium peroxide and carbon dioxide, since no sodium percarbonate can be prepared by electrolysis, differs in its behaviour towards potassium iodide, and therefore in constitution, from electrolytic potassium percarbonate; consequently Riesenfeld and Mant prepared a potassium percarbonate from potassium peroxide and carbon dioxide, and found that it possessed the composition  $\text{K}_2\text{C}_2\text{O}_6$ , and resembled  $\text{Na}_2\text{C}_2\text{O}_6$  in chemical reactivity. Thus two isomeric potassium percarbonates were found to exist: one prepared by electrolysis which was believed to have the constitution  $\text{KO CO O O CO OK}$ , and the other prepared from potassium peroxide and carbon dioxide to which the constitution  $\text{KO O CO O O CO OK}$  was attributed, and which resembled the only existing sodium percarbonate of the same empirical composition.

To the compound  $\text{Na}_2\text{CO}_4$  the constitution  $\text{NaO O CO O Na}$  was attributed, and consequently electrolytic  $\text{K}_2\text{C}_2\text{O}_6$  and  $\text{Na}_2\text{CO}_4$  stand in the same relation to one another as perdis- and permono-sulphates. Thus:



Barium percarbonate is formed when carbon dioxide gas is passed through barium peroxide suspended in water; for hydrogen peroxide only appears in quantity in the solution after a considerable time. The gas is first absorbed to form the percarbonate, and when no barium peroxide remains the liquid becomes acid, and the percarbonate is hydrolysed with the liberation of hydrogen peroxide.<sup>1</sup>

Percarbonic acid itself is very unstable, but if electrolytic potassium percarbonate is decomposed by phosphoric acid in presence of ether, the liberated percarbonic acid dissolves in the ether, and from this ethereal solution the potassium salt may be regenerated by adding potassium hydroxide.

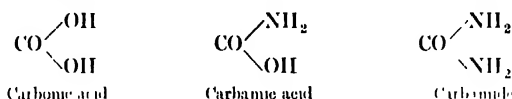
Percarbonic acid may be estimated by decomposing its salts with dilute sulphuric acid, and titrating the liberated hydrogen peroxide with permanganate.

<sup>1</sup> E. Merck, *D.R.P.* 179,771, December 1906, also *D.R.P.* 178,019 and 179,826.



## AMINO-DERIVATIVES OF CARBONIC ACID

When the hydroxyl groups of carbonic acid are replaced successively by amino- ( $\text{NH}_2$ ) groups there are produced respectively carbamic acid and carbamide.



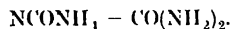
**Carbamic Acid**,  $\text{HO}\cdot\text{CO}\cdot\text{NH}_2$ , the half-amide of carbonic acid, is unknown, but several of its salts exist, the most important of which is ammonium carbamate,  $\text{NH}_4\text{O}\cdot\text{CO}\cdot\text{NH}_2$ . This salt is formed by the union of carbon dioxide with ammonia:



which is best effected by passing the mixed, dry gases through absolute alcohol. Ammonium carbamate also occurs, together with ammonium bicarbonate, in commercial carbonate of ammonia, prepared by sublimation when a moistened mixture of calcium carbonate and ammonium sulphate is heated; it gradually sublimates at atmospheric temperature from this compound, and is frequently deposited in transparent prisms upon the neck of the bottle containing the commercial salt. The carbamate may also be obtained from the commercial salt by acting upon it for thirty or forty hours with saturated solution of ammonia at  $20^\circ$ – $25^\circ\text{C}^\circ$ ; but dilute ammonia solution, like water, converts carbamate in solution into normal carbonate. When vaporised, ammonium carbamate is completely dissociated into ammonia and carbon dioxide. This is shown by the vapour density,<sup>2</sup> which is 0.892 (air = 1) between  $37^\circ\text{C}.$  and  $100^\circ\text{C}.$  Recombination on cooling is slow, owing to the necessary intramolecular change. Sodium and potassium carbamates and a basic calcium salt,  $\text{NH}_2\cdot\text{CO}\cdot\text{OCa}(\text{OH})$ , are known. Ethyl carbamate,  $\text{NH}_2\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$ , is methane.

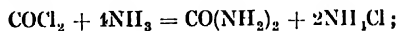
**Carbamide**, or **Urea**,  $\text{CO}(\text{NH}_2)_2$ , the amide of carbonic acid, may be briefly noticed here.

Urea was discovered by Rouelle in 1773, investigated by Fourcroy and Vauquelin in 1790, and prepared from ammonium cyanate by Wohler in 1828<sup>3</sup>:



Urea may be prepared from urine by evaporation and extraction of the residue with alcohol; or by precipitating from the concentrated urine the sparingly soluble nitrate or oxalate, which are subsequently decomposed by potassium carbonate and chalk respectively.

Like other amides, carbamide can be prepared by the action of ammonia on the corresponding acid chloride, which is carbonyl chloride or phosgene,  $\text{COCl}_2$ :

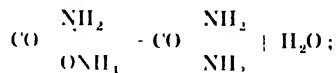


<sup>1</sup> Divers, *Trans. Chem. Soc.*, 1873, 23, 215.

<sup>2</sup> Naumann, *Annalen*, 1860, 150, 1.

<sup>3</sup> Wohler, *Pogg. Annalen*, 1828, 12, 253.

urea may also be prepared from ammonium carbamate, which loses water when heated to 130° to 140° C. :



but it is best obtained from ammonium cyanate according to the transformation discovered by Wöhler. For this purpose potassium cyanate is first prepared by oxidising potassium cyanide by fusing it with red lead, or by the oxidation of potassium ferrocyanide by means of potassium dichromate. The potassium cyanate is then extracted with water and evaporated with its equivalent of ammonium sulphate; and from the mixture of potassium sulphate and urea which forms the residue the latter is extracted by means of alcohol, from which it may be crystallised.

Urea crystallises in quadrate prisms which melt at 132° C. and decompose at a higher temperature. The transformation of ammonium cyanate into urea is a reversible reaction, and the mechanism of the change has been the subject of much research and theorising.<sup>1</sup>

Urea is very soluble in hot and cold water—it dissolves in 5 parts of cold and in 1 part of boiling alcohol, but is practically insoluble in ether.

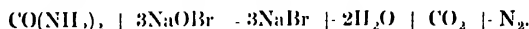
Being the amide of a weak acid, urea has distinctly basic properties, although its aqueous solution is neutral in reaction.

*Urea hydrochloride*,  $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$ , is formed with the evolution of heat by the union of HCl gas with urea in absence of water. It forms crystals which are completely decomposed by water.

*Urea nitrate*,  $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ , though moderately soluble in water, is almost insoluble in nitric acid, and is therefore formed as a crystalline precipitate when this acid is added to a sufficiently concentrated solution of urea; the formation of this salt is a characteristic reaction of urea.

*Urea oxalate*,  $2\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{C}_2\text{O}_4$ , crystallises in monocline plates when concentrated solutions of urea and oxalic acid are mixed.

**Reactions of Urea.** When urea is heated above its melting-point it loses ammonia and is converted into biuret,  $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , and other products.<sup>2</sup> When biuret is dissolved in alkali and a drop of dilute copper sulphate solution is added to the liquid, a purple colour is produced. This reaction constitutes a valuable test for urea. Like other amides, urea is not decomposed by cold alkali, but when warmed with alkali hydroxide solution it forms alkali carbonate with evolution of ammonia. Urea behaves similarly to ammonium salts towards hypochlorite or hypobromite and nitrite solutions, *i.e.* its nitrogen is evolved in the gaseous state. Thus with hypobromite solution the following reaction takes place :



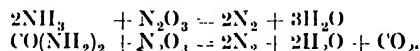
The measurement of the nitrogen evolved in this reaction serves to

<sup>1</sup> Walker and Hamblly, *Trans. Chem. Soc.*, 1895, 67, 749; Waller and Kay, *ibid.*, 1897, 71, 489; Goldschmidt, *Zeitsch. Elektrochem.*, 1905, 11, 5, 1 scales; *Chem. Zeit.*, 1911, 35, 595; Chattaway, *Trans. Chem. Soc.*, 1912, 101, 170; Wheeler, *J. Amer. Chem. Soc.*, 1912, 34, 1269; Lewis and Burrows, *J. Amer. Chem. Soc.*, 1912, 34, 1515; E. A. Werner, *Trans. Chem. Soc.*, 1913, 103, 1010, 2275.

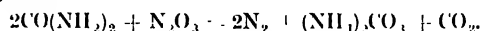
<sup>2</sup> E. A. Werner, *Trans. Chem. Soc.*, 1913, 103, 2275.

estimate urea, though experience shows that the volume of nitrogen liberated corresponds to only 92 per cent. of the urea.

The similarity between the reactions of ammonia and urea towards nitrous acid is shown by the equations :



The second equation represents the reaction between warm solutions of urea and nitrite, if the solutions are cold only half the amino-nitrogen reacts with the nitrite and the remainder appears as ammonium carbonate, thus :

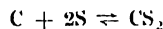


Concentrated hydrochloric acid converts urea into carbon dioxide and ammonium chloride, evanic acid being an intermediate product.<sup>1</sup>

### CARBON DISULPHIDE, CS<sub>2</sub>, AND ITS DERIVATIVES

Carbon disulphide is formed when carbon and sulphur are heated together, and is consequently produced when coal containing iron pyrites is distilled. In this way it was discovered accidentally by Lampadius<sup>2</sup> in 1796, and again by Clément and Desormes in 1802, who, after at first supposing it to be a compound of hydrogen and sulphur, subsequently proved that it contained only carbon and sulphur. It remained, however, for Vauquelin fully to elucidate the nature of this compound by showing that when its vapour is passed over heated copper, carbon and copper sulphide result. Besides occurring in small quantity in coal-gas, from which it should be eliminated, carbon disulphide is also found in crude petroleum and in mustard oil.

**Preparation.** Carbon disulphide is prepared by passing sulphur vapour over red-hot charcoal. This may be done on a small scale by heating pieces of charcoal contained in a combustion tube placed in a furnace slightly tilted. To the lower end of the tube a Liebig's potash bulb is attached, and is immersed in ice. Small pieces of sulphur are introduced into the upper end of the tube, which is then closed with a cork. Sulphur vapour passes over the red-hot charcoal and impure carbon disulphide, containing sulphur in solution, is gradually formed and collects in the cooled receiver. The reversible reaction



has been studied at 800°–1100° C. by Koref.<sup>3</sup>

For the manufacture of carbon disulphide on a large scale the charcoal is contained in a large vertical cast-iron cylinder 10 to 12 ft. high and 1 to 2 ft. in diameter. This is surrounded by brickwork and heated by a fire beneath, the sulphur being introduced through a hopper connected with a side tube at the base of the cylinder. The carbon disulphide vapour is led away from the top of the cylinder by a pipe, the end of which dips under water, where most of the product condenses. Beyond the water-condenser is a series of tubes in which

<sup>1</sup> See Under (Ureic Acid)

<sup>2</sup> Lampadius, *Gehlen's Allg. J. Chem.*, 1796, **11**, 192

<sup>3</sup> Koref, *Zeitsch. anorg. Chem.*, 1910, **66**, 73.

the condensation is completed and the compound thus freed from hydrogen sulphide, which is subsequently absorbed in slaked lime.

In a recent American process<sup>1</sup> carbon disulphide is prepared in an electric furnace which produces 3000 kilograms *per diem*.

Crude carbon disulphide has a very offensive odour due to the presence of organic sulphur compounds; sulphur, also, is contained in solution, which is left behind on redistillation. Organic impurities are eliminated by distilling over fat, which retains them. Contact with mercury, corrosive sublimate, solid potassium permanganate, and fuming nitric acid serves the same purpose.

**Physical Properties.** Pure carbon disulphide is a colourless, highly refractive liquid with a pleasant aromatic smell resembling that of chloroform. Its density at 0° C., according to Thorpe,<sup>2</sup> is 1.2923; according to Wullner<sup>3</sup> the density at *t* can be calculated from the formula  $D_0 = 1.29366 - 0.001506t$ . The vapour density<sup>4</sup> of CS<sub>2</sub> is 2.68, whilst that corresponding to the molecular weight would be 2.62.

The boiling-point<sup>5</sup> at 760 mm. pressure is 46.25° C., according to Regnault.<sup>6</sup> The vapour pressures at different temperatures are as follow.

Temp. ° C.	Vapour Pressure mm.	Temp. ° C.	Vapour Pressure mm.	Temp. ° C.	Vapour Pressure mm.
-20	47.3	40	617.53	100	3325.15
-10	79.14	50	857.07	110	4164.06
0	127.91	60	1161.51	120	5148.79
10	198.46	70	1522.09	130	6291.60
20	298.03	80	2022.53	140	7603.96
30	431.62	90	2619.08	150	9095.91

The constants<sup>7</sup> for van der Waals' equation are :

$$a = 0.02166; b = 0.003209,$$

and the critical temperature and pressure, respectively :

$$277.68^\circ \text{C. and } 78.11 \text{ atmospheres}$$

At very low temperatures CS<sub>2</sub> solidifies to a crystalline mass which melts at -110° C.<sup>8</sup> or -108.6° C.<sup>9</sup> or -112.8° C.<sup>10</sup> The fusion curve, showing the connection between pressure and melting-point, has been determined by Tammann.<sup>11</sup>

<sup>1</sup> Taylor, *Zeitsch. Elektrochem.*, 1903, 9, 679, 982

<sup>2</sup> Thorpe, *Trans. Chem. Soc.*, 1880, 37, 361

<sup>3</sup> Wullner, *Progr. Annalen*, 1868, 133, 19

<sup>4</sup> V. and C. Meyer, *Ber.*, 1879, 11, 2257

<sup>5</sup> Von Unruh, *Zeitsch. anorg. Chem.*, 1902, 32, 407

<sup>6</sup> Regnault, *Mém. de l'Acad.*, 1862, 26, 339

<sup>7</sup> Hannay, *Proc. Roy. Soc.*, 1882, 33, 314

<sup>8</sup> Wroblewski and Olszewski, *Compt. rend.*, 1883, 96, 1112

<sup>9</sup> Cariani and Coppadoto, *Zeitsch. physikal. Chem.*, 1903, 44, 379

<sup>10</sup> Holborn and Wien, *Zeitsch. physikal. Chem.*, 1903, 44, 80

<sup>11</sup> Tammann, *Zeitsch. physikal. Chem.*, 1912, 81, 187

The total heat of vaporisation <sup>1</sup> ( $\lambda$ ) of CS<sub>2</sub> at 0° into vapour at  $t^\circ$  is given by the expression :

$$\lambda = 89.5 + 0.16993t - 0.0010161t^2 + 0.0000033215t^3;$$

Calories per kg

whilst the latent heat of vaporisation ( $r$ ) of liquid at  $t^\circ$  into vapour at  $t^\circ$  is given thus :

$$r = 89.5 - 0.06530t - 0.0010979t^2 + 0.0000031215t^3.$$

Calories per kg

The constant K for the molecular rise of boiling-point of carbon disulphide <sup>2</sup> is 23.7. The specific heat of liquid carbon disulphide is <sup>3</sup> :

$$C_{liq} = 0.2352 + 0.000162t,$$

and of the vapour at 86°-190° C is :

$$C_{vap} = 0.1596 \text{ (Regnault),}$$

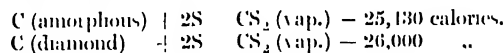
whilst the ratio  $\frac{C_p}{C_l}$  at 99.7° C <sup>4</sup> is 1.234.

Carbon disulphide possesses high optical refractive and dispersive power, in which it is exceeded only by methylene iodide, bromonaphthalene, and phenyl-mustard oil. On this account it is used for filling hollow glass prisms for producing spectra.

The following are the refractive indices <sup>5</sup> for lines of different wave lengths of the visible spectrum at 0° C. and 20° C. :

Wave Length	Refractive Index at 0° C.	Refractive Index at 20° C.
589.31 $\mu\mu$ (D)	1.64362	1.62761
533.85 ..	1.65508	1.63877
480.01 ..	1.67131	1.65166
441.59 ..	1.68850	1.67135
394.11 ..	1.71989	1.70180

Carbon disulphide is an endothermic compound, its heats of formation <sup>6</sup> as vapour from rhombic sulphur and amorphous carbon and diamond being respectively :



Carbon disulphide is an excellent solvent for fats and resins, and is employed technically for the extraction of vegetable fats and oils, and for removing fat from wool. It also dissolves rubber, camphor, and other organic substances, as well as iodine, sulphur, and phosphorus.

Carbon disulphide is slightly soluble in water, its solubility diminish-

<sup>1</sup> Winkelmann, *Ann. Physik*, 1880, 9, 208, 358

<sup>2</sup> Beckmann, *Zeitsch. physikal. Chem.*, 1890, 6, 437

<sup>3</sup> Regnault, *Mém. de l'Acad.*, 1862, 26, 1, 262

<sup>4</sup> Stevens, *Ann. Physik*, 1902, [iv], 7, 285

<sup>5</sup> Flatow, *Ann. Physik*, 1903, [iv], 12, 85

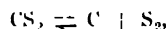
<sup>6</sup> Thomsen, *Zeitsch. physikal. Chem.*, 1905, 52, 348

ing with rising temperature like that of a gas. One hundred cubic centimetres of water dissolve the following quantities of carbon disulphide at the corresponding temperatures <sup>1</sup>:

Temp. ° C. . . . .	0	10	20	30	40	50
Gram CS <sub>2</sub> . . . . .	0.204	0.191	0.179	0.155	0.111	0.014

100 c.c. of carbon disulphide dissolve 0.974 c.c. of water <sup>2</sup> at 22° C.

**Chemical Properties.** Carbon disulphide is not easily decomposed by heat, and no change is observed when it is passed through a tube at 100° C. Decomposition may be started by detonation with mercury fulminate, but is not propagated through the vapour <sup>3</sup>. Dissociation according to the reaction



which is considerable at high temperature, is promoted by the presence of metals with which the sulphur can combine, the carbon separating as graphite. A lower sulphide of carbon, C<sub>2</sub>S, or CS, has been supposed to be formed <sup>4</sup>.

The electric arc, electric sparks, and the silent electric discharge decompose carbon disulphide; in the latter case it has been shown by Dewar and Jones <sup>5</sup> that the lower sulphide CS is formed, together with free sulphur.

Carbon disulphide burns in the air with a blue flame, producing carbon dioxide and sulphur dioxide. Moisture is not necessary to combustion <sup>6</sup>. The vapour undergoes phosphorescent combustion in oxygen, thus showing "chemiluminescence" below its temperature of ignition. This phenomenon may begin at 230° C. and persist until the temperature falls below 200° C., although the temperature of ignition is about 260° C. Owing, however, to its gradual or "silent" combustion, with the accompanying chemiluminescence, no definite ignition temperature can be assigned to this substance. In this property it resembles carbon monoxide, but differs from the hydrocarbons. The flame of carbon disulphide shows a continuous spectrum and is strongly actinic.

The following facts with regard to the combustion of carbon disulphide have been established by Dixon and Russell <sup>7</sup>. The combustion is not preceded by a decomposition of the substance into its elements, so that no carbon is separated; the reaction cannot be expressed by a single equation. With excess of oxygen the products are carbon dioxide, sulphur dioxide, sulphur trioxide, and free sulphur; and in the explosion wave there occur carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide. With insufficient oxygen the products are carbon dioxide, sulphur dioxide, carbon monoxide, carbonyl sulphide, and carbon disulphide. Limitation of oxygen reduces the sulphur dioxide formed, but even the minimum amount of oxygen is always divided between the carbon and sulphur.

Carbon disulphide forms an explosive mixture with air or oxygen. The explosive limits with oxygen are 1 volume of oxygen to 1½ volume

<sup>1</sup> Chancel and Parmentier, *Compt. rend.*, 1885, 100, 773

<sup>2</sup> *Zeit. Ber.*, 1898, 31, 2669

<sup>3</sup> Dixon and Russell, *Trans. Chem. Soc.*, 1889, 75, 612

<sup>4</sup> Arcetowski, *Zeitsch. anorg. Chem.*, 1895, 8, 314

<sup>5</sup> Dewar and Jones, *Proc. Roy. Soc.*, 1910, A, 83, 408, 526.

<sup>6</sup> Breton Baker, *Phil. Trans.*, 1888, 179, 582.

<sup>7</sup> Dixon and Russell, *Trans. Chem. Soc.*, 1899, 75, 612

of carbon disulphide vapour, and 6-7 volumes of oxygen to 1 volume of carbon disulphide vapour.

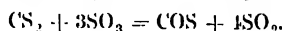
When a mixture of carbon disulphide vapour and air is burnt in a Smithell's separator the interconal gases are found to consist of equal volumes of sulphur dioxide and carbon monoxide, with sulphur vapour and some unchanged carbon disulphide, together with small quantities of carbonyl sulphide and carbon dioxide.

Apart from combustion, carbon disulphide can be oxidised and reduced, and also made to undergo additive reactions, the most prominent of which is its combination with alkalis to form thio- or sulpho-salts.

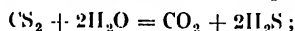
*Oxidation of Carbon Disulphide.*—Hypochlorite solution converts carbon disulphide into carbonate and sulphate,<sup>1</sup> thus :



In the absence of alkali, oxidation—as, for instance, by permanganate solution, bromine water, nitric or iodic acid—involves the separation of sulphur. Sulphur trioxide produces carbonyl sulphide, thus<sup>2</sup> :



Water and aqueous alkalis hydrolyse carbon disulphide at 150° C., thus<sup>3</sup> :

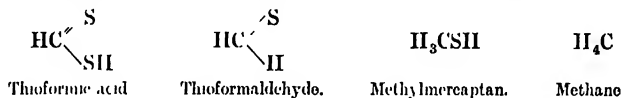


and baryta water, when heated with carbon disulphide in an atmosphere of nitrogen, brings about a similar change :



whilst the hydrosulphide is converted by contact with air into sulphate.<sup>4</sup>

*Reduction of Carbon Disulphide.*—Just as by the reducing action of hydrogen on carbon dioxide formic acid, formaldehyde, methyl alcohol, and methane may be directly or indirectly produced, so similarly from carbon disulphide the following compounds should result :



Thioformic acid is unknown, but thioformaldehyde, polymerising to tri-thioformaldehyde,  $(\text{H}_2\text{CS})_3$ , results from the reduction of carbon disulphide by nascent hydrogen<sup>5</sup>; methyl mercaptan cannot be obtained directly from carbon disulphide, but methane is commonly prepared by passing its vapour, together with hydrogen sulphide, over heated copper :



**Thio-acids and Salts derived from Carbon Disulphide.**—Carbon disulphide, like the dioxide, is the anhydride of a feeble acid : thiocarbonic acid,  $\text{H}_2\text{CS}_2$ . Moreover, between carbonic and thiocarbonic acids a

<sup>1</sup> Ridsema, *Chem. Zentr.*, 1904, ii, 1495.

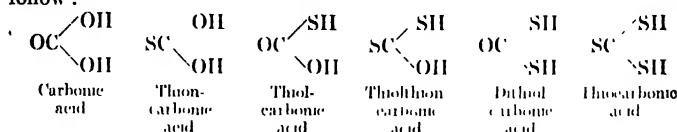
<sup>2</sup> Armstrong, *Ber.*, 1869, 2, 712.

<sup>3</sup> Schlaglenhaufen, *J. Pharm.*, 1856, [iii], 29, 401.

<sup>4</sup> Clabiel and Paimentier, *Compt. rend.*, 1884, 99, 892.

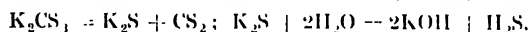
<sup>5</sup> Girard, *Compt. rend.*, 1856, 43, 396.

number of intermediate acids are capable of existence. They are as follow :



It was discovered by Berzelius that when carbon disulphide is brought into contact with sodium sulphide solution the former dissolves, producing a solution from which alcohol precipitates sodium thiocarbonate,  $\text{Na}_2\text{CS}_3$ , as a yellowish-brown oil. From this salt dilute hydrochloric acid separates the free acid,  $\text{H}_2\text{CS}_3$ , as a yellow oil, which possesses a very disagreeable odour and is decomposed by heat into  $\text{CS}_2$  and  $\text{H}_2\text{S}$ . Thus it is noteworthy that  $\text{H}_2\text{CS}_3$  is more stable than  $\text{H}_2\text{CO}_3$ , doubtless because  $\text{CS}_2$  is a liquid while  $\text{CO}_2$  is a gas.

*Decomposition of Potassium Thiocarbonate.* It has been shown by Tarugi and Magri<sup>1</sup> that when a solution of potassium thiocarbonate is boiled in an atmosphere of nitrogen the following changes take place :



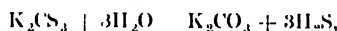
In presence of air or oxygen, however, the reaction is as follows :



and in an atmosphere of carbon dioxide



These authors deny that the reaction

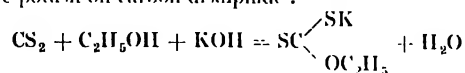


inherently improbable, can take place.

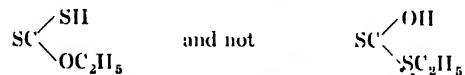
Salts and esters of the intermediate acids are known, being prepared from carbon disulphide or carbon oxysulphide.

Thiocarbonic acid,  $\text{HS CO OH}$ , yields carbon oxysulphide,  $\text{COS}$ , by decomposition; the esters yield alcohols or mercaptans when saponified, according to whether the alkyl group is attached to oxygen or to sulphur; by this means the constitutions of the acids are established.

It may be observed that thion- and thiol-carbonic acids are isomeric, as well as thiothion- and dithiol-carbonic acids. Ethyl thiothion-carbonic acid is **xanthic** or **xanthogenic acid**. Its potassium salt, which is yellow and has a disagreeable smell, is prepared by the action of alcoholic potash on carbon disulphide :



The free acid decomposes at  $24^\circ \text{C}$ . into ethyl alcohol and carbon disulphide; hence its constitution is known to be :



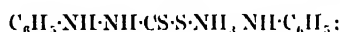
<sup>1</sup> Tarugi and Magri, *Gazzetta*, 1909, 39, 1 405



Carbon disulphide also combines with tertiary amines<sup>1</sup> and phosphines, forming crystalline substances, the most important of which is a red compound with triethylphosphine,  $\text{CS}_2\text{P}(\text{C}_2\text{H}_5)_3$ , to which the constitution  $\text{CS} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{P}(\text{C}_2\text{H}_5)_3$  is attributed.<sup>2</sup>



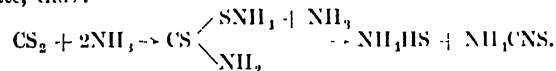
**Detection and Estimation of Carbon Disulphide.**—Carbon disulphide may be detected by means of the red, crystalline compound it forms with triethylphosphine, and the white compound with phenylhydrazine<sup>3</sup>:



also by its conversion into thiocarbonate, which gives a yellow precipitate with silver nitrate, and a red precipitate with lead nitrate, each of which quickly turns black by conversion into sulphide.

Minute quantities of carbon disulphide can also be detected by producing one of the dithiotimercuric salts of the type  $\text{HgX}_2 \cdot 2\text{HgS}$ , which form characteristic crystalline precipitates when dilute aqueous solutions of mercuric salts are heated on the water-bath with carbon disulphide.<sup>4</sup>

Carbon disulphide is estimated by solution in alcoholic potash with formation of xanthate, followed by titration with standard copper sulphate,<sup>5</sup> or with permanganate solution, which oxidises the xanthate to sulphate.<sup>6</sup> A third method depends upon the fact that ammonia converts carbon disulphide into a mixture of hydrosulphide and thiocyanate, thus:

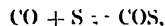


The hydrosulphide may then be titrated with ammoniacal zinc solution.<sup>7</sup>

Carbon disulphide may be estimated gravimetrically by treatment with baryta water, so that sulphide is produced, which is then oxidised and weighed as  $\text{BaSO}_4$ .<sup>8</sup>

**Uses of Carbon Disulphide.**—Besides its employment as a solvent, to which reference has been made, carbon disulphide is used in the vulcanising of india-rubber, for the preparation of ammonium thiocyanate, and of numerous organic compounds, including a number of dyes containing sulphur, as well as for the prevention of phylloxera in vines.

**Carbonyl Sulphide (Carbon Oxy-sulphide)** ( $\text{COS}$ )—Carbonyl sulphide, a gas discovered by Thén,<sup>9</sup> is formed synthetically when a mixture of carbon monoxide and sulphur vapour is passed through a hot tube. The reaction is reversible:



<sup>1</sup> Blenhard, *Compt. rend.*, 1878, 87, 1040.

<sup>2</sup> Hofmann, *Annalen Suppl.*, 1861, 1, 26, 59.

<sup>3</sup> Fischer, *Annalen*, 1877, 190, 114, Lieberman and Seyewitz, *Ber.*, 1891, 24, 788; Busch, *Ber.*, 1891, 27, 2307.

<sup>4</sup> Deniges, *Bull. Soc. chim.*, 1915, [iv], 17, 353, 359.

<sup>5</sup> Macagno, *Gazzetta*, 1880, 10, 485.

<sup>6</sup> Schmitz-Dumont, *Chem. Zeit.*, 1897, 21, 487.

<sup>7</sup> Goldberg, *Zeitschr. angew. Chem.*, 1899, 75.

<sup>8</sup> Chancel and Parmentier, *Compt. rend.*, 1884, 99, 892.

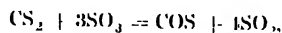
<sup>9</sup> Thén, *Annalen Suppl.*, 1867, 5, 236.

## CARBON AND ITS COMPOUNDS

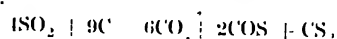
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so that the proportion of carbonyl sulphide formed depends upon the temperature and rate of passage of the gas.

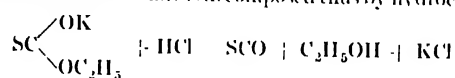
Carbonyl sulphide results similarly from carbon disulphide and sulphur trioxide, thus :



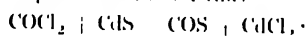
and also when sulphur vapour and air are passed over a red-hot mixture of clay and carbon,<sup>1</sup> as well as when sulphur dioxide is passed over red-hot carbon<sup>2</sup> :



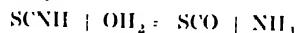
Some thiocarbonates yield carbonyl sulphide by decomposition; e.g. potassium ethylthiocarbonate is decomposed thus by hydrochloric acid<sup>3</sup>.



Sulphur may be substituted for chlorine in carbonyl chloride by means of cadmium sulphide at 270° C., thus :



but the most important method of preparing carbonyl sulphide consists in the decomposition of a thiocyanate with dilute acid, the liberated thiocyanic acid being hydrolysed thus :



To a cooled mixture of 5 volumes of sulphuric acid and 4 volumes of water potassium thiocyanate is added, and the gas is evolved at about 20° C., together with hydrocyanic acid, formic acid, and carbon disulphide. The acid vapours are removed by passing the gas through strong alkali, and the carbon disulphide is absorbed in a mixture of triethylphosphine, pyridine, and nitrobenzene. After drying with sulphuric acid the gas may be further purified by liquefaction or absorption in toluene.<sup>4</sup>

**Physical Properties.** Carbonyl sulphide is a colourless gas possessing a resinous smell, but is said to be odourless when pure. Its density at 0° C. is 2.1046, that calculated from the molecular weight being 2.0749. That this compound stands about midway between carbon dioxide and carbon disulphide in physical properties as well as in chemical composition is shown in the following table :

	Critical Temp. °C.	Boiling point (1 atm.)	Vapour pressure at 0° Atmospheres	Heat of formation Calories
Carbon dioxide	31.1	-80	35.4	97
Carbonyl sulphide	105	-47.5	12.5	37
Carbon disulphide	275	46	0.17	-25.4

<sup>1</sup> Gautier, *Compt. rend.*, 1888, 107, 911

<sup>2</sup> Berthelot, *Compt. rend.*, 1883, 96, 208

<sup>3</sup> Salomon, *J. prakt. Chem.*, 1872, 5, 476

<sup>4</sup> Hofmann, *Annalen Suppl.*, 1861-2, 1, 26, 59, Hempel, *Zeitsch. angew. Chem.*, 1901, 14, 865.

Liquid carbonyl sulphide is colourless and highly refractive; it dissolves sulphur and mixes with various organic liquids.

The gas is somewhat soluble in water, its solubilities at different temperatures being as follow:

Temperature ° C.	0°	5°	10°	15°	20°	25°	30°
1 vol. water dissolves	1.333	1.056	0.835	0.677	0.561	0.468	0.403

It is found in solution in certain mineral waters; e.g. those of Harkány and Paráđ in Hungary.

The following thermal values are given by Thomsen<sup>1</sup>:

Heat of combustion = 131.010 calories.

Heats of formation:

C (amorph.) + S (rhomb.) + O = COS + 37,320 calories.

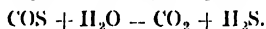
CO + S = COS + 8.030 calories.

Berthelot,<sup>2</sup> however, gives a value for the heat of formation about half that obtained by Thomsen:

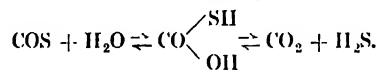
C (amorph.) + S (rhomb.) + O = COS + 19.600 calories.

*Chemical Properties.* - Carbonyl sulphide may be ignited by means of a glowing splinter of wood, and burns with a blue, slightly luminous flame. With air it forms a mixture which is slightly explosive except when quite dry.<sup>3</sup> The explosive limits lie between 11.9 and 28.5 per cent. of carbonyl sulphide.<sup>4</sup> A white-hot platinum wire completely decomposes the gas into carbon monoxide and sulphur.

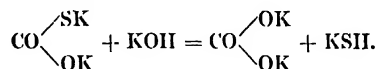
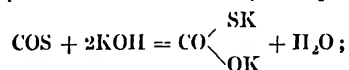
Water slowly decomposes carbonyl sulphide, thus:



According to Buchbock<sup>5</sup> the reaction proceeds in two stages, thiocarbonic acid being an intermediate product:



Alkali solutions form salts of the same acid, which, however, soon decompose into carbonate and hydrosulphide:



Alcoholic potash forms, in all probability, potassium ethylthion-

carbonate,<sup>6</sup>  $\text{CS} \begin{array}{l} \text{OK} \\ \text{OC}_2\text{H}_5 \end{array}$ , whence carbonyl sulphide is liberated again

<sup>1</sup> Thomsen, *Ber.*, 1883, 16, 2619. *Zeitsch. physikal. Chem.*, 1905, 52, 348.

<sup>2</sup> Berthelot, *Ann. Chim. Phys.*, 1879, [v], 17, 129.

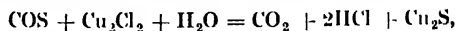
<sup>3</sup> E. J. Russell, *Trans. Chem. Soc.*, 1900, 77, 361.

<sup>4</sup> Hempel, *Zeitsch. angew. Chem.*, 1901, 14, 865.

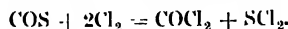
<sup>5</sup> Buchbock, *Zeitsch. physikal. Chem.*, 1897, 23, 123; 1900, 77, 361.

<sup>6</sup> Bender, *Annalen*, 1868, 148, 138.

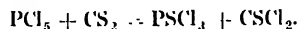
by acid. Heated mercury, copper, iron, and silver remove sulphur from carbonyl sulphide; cuprous chloride reacts thus:



and chlorine forms phosgene and sulphur dichloride:



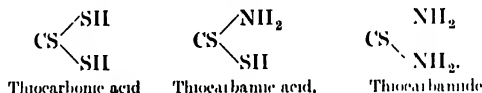
**Thiocarbonyl Chloride,  $\text{CSCl}_2$ .**—Thiocarbonyl chloride is formed by the prolonged action of dry chlorine on carbon disulphide,<sup>1</sup> and by heating phosphorus pentachloride and carbon disulphide together in sealed tubes<sup>2</sup> at  $100^\circ\text{C}$  :



It may also be obtained by the reduction, by tin and hydrochloric acid, of  $\text{CSCl}_4$ , which is a liquid boiling at  $149^\circ\text{C}$ , formed by the action of chlorine on carbon disulphide in presence of a little iodine.

Thiocarbonyl chloride is a strongly smelling liquid of density 1.5085 at  $15^\circ\text{C}$  and boiling at  $73.5^\circ\text{C}$ . It is slowly decomposed by water.<sup>3</sup>

**Amino-derivatives of Thiocarbonic Acid.**—As carbamic acid and carbamide are related to carbonic acid, so are thiocarbamic acid and thiocarbamide related to thiocarbonic acid:



**Thiocarbamic acid**, or, more definitely, *thiothiocarbamic acid*,<sup>4</sup>  $\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{CS} \\ \diagdown \\ \text{SH} \end{array}$ , is obtained from its ammonium salt, which is formed by

the combination of carbon disulphide with dry ammonia in presence of alcohol, whence the salt crystallises in prisms. Hydrochloric acid separates the acid from an aqueous solution of its ammonium salt in the form of an unstable oil which crystallises<sup>5</sup> below  $10^\circ\text{C}$ , smells of hydrogen sulphide, is acid in reaction, and easily decomposes into  $\text{H}_2\text{S}$  and  $\text{CNHS}$ .

**Thiocarbamide, Thiourea,  $\text{CS}(\text{NH}_2)_2$ .**—Thiourea is formed by heating ammonium thiocyanate<sup>6</sup> to  $110^\circ\text{C}$ , this salt undergoing an isomeric change analogous to that produced in ammonium cyanate by heat:



At the same time some guanidine thiocyanate,<sup>7</sup>  $\text{NH}:\text{C}(\text{NH}_2)_2\cdot\text{HSCN}$ , is produced, though a larger proportion of this latter substance is formed at  $170^\circ\text{--}180^\circ\text{C}$ . The thiourea is freed from guanidine thiocyanate and unchanged ammonium thiocyanate by cold water, in which the thiourea is but sparingly soluble; it is then purified by recrystallisation from water.

<sup>1</sup> Kolbe, *Annalen*, 1843, 45, 41

<sup>2</sup> Carius, *Annalen*, 1859, 112, 193

<sup>3</sup> Klason, *Ber.*, 1887, 20, 2378

<sup>4</sup> Zeise, *Annalen*, 1843, 48, 95, Debus, *Annalen*, 1850, 73, 26

<sup>5</sup> Mulder, *J. prakt. Chem.*, 1867, 101, 401; 1868, 105, 178.

<sup>6</sup> Reynolds, *Trans. Chem. Soc.*, 1855, 8, 1

<sup>7</sup> Volhard, *Ber.*, 1874, 7, 92, *J. prakt. Chem.*, 1874, [11], 9, 6

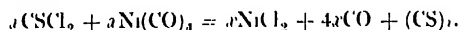
A better method of preparation consists in heating carbon disulphide<sup>6</sup> (6 grams) with ammonium carbonate (8 grams) in a sealed tube at 160° C., when the yield is quantitative.<sup>1</sup>

Thiourea crystallises in rhombic prisms, and dissolves in eleven times its weight of cold water. When heated with water to 140° C. it reverts to ammonium thiocyanate. It forms salts analogous to those of urea; the most characteristic of these is the nitrate,  $\text{CS}(\text{NH}_2)_2 \cdot \text{HNO}_3$ .

**Perthiocarbonates.** -It was seen (p. 135) that there are two classes of percarbonates, one obtained by the electrolytic oxidation of carbonates, the other by the combination of hydrogen peroxide with carbonates, or of carbon dioxide with peroxides. Alkali perthiocarbonates, e.g.  $\text{Na}_2\text{CS}_4$ , exist corresponding to the latter kind of percarbonates. They are formed by the combination of carbon disulphide with alkali disulphides, with which this substance unites more readily than with the monosulphides, and also by the direct combination of thiocarbonates with sulphur.<sup>2</sup> There is no analogy to this latter method of preparation in the case of percarbonate; and this fact illustrates the superior chain-forming power of sulphur as compared with oxygen atoms.

**Lower Sulphides of Carbon.** -Besides the well-known carbon disulphide, two other sulphides of carbon are known -CS and  $\text{C}_3\text{S}_2$ , and have recently been prepared and studied in some detail.

**Carbon Monosulphide, CS.** The first indication of the existence of the sulphur analogue of carbon monoxide was the observation of Losanitsch and Jovitschitsch<sup>3</sup> that carbon disulphide is decomposed by the silent electric discharge in presence of hydrogen or carbon monoxide with the formation of a lower sulphide supposed to be CS; Thomsen<sup>4</sup> also found that when nitrogen saturated with carbon disulphide vapour is passed repeatedly over heated copper, the copper removes some sulphur from the disulphide, leaving the monosulphide. More recently Dewar and H. O. Jones<sup>5</sup> found that thiocarbonyl chloride reacts rapidly with nickel carbonyl at the ordinary temperature according to the equation:



When nickel chloride is extracted by water from the solid product, a brown substance remains which by analysis is shown to have the empirical composition represented by the formula CS, but which, on account of its being a non-volatile solid, must be a polymer  $(\text{CS})_x$ . The same product was always obtained, although the conditions of its formation were varied, and after purification and drying it had a density of about 1.6 in the finely divided state and of 1.83 after compression.

Polymerised carbon monosulphide gives a purplish-brown solution with concentrated sulphuric acid, from which the unchanged substance is reprecipitated on pouring into water. Aqueous and alcoholic solutions of ammonia, ammonium sulphide, and potassium hydroxide, sulphide, and hydrosulphide, also give deep brown solutions from which the monosulphide is precipitated unchanged by acid. The solid is

<sup>1</sup> Inghillen, *Gazzetta*, 1909, 39, 1, 634

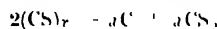
<sup>2</sup> Gélus, *Compt. rend.*, 1875, 81, 282

<sup>3</sup> Losanitsch and Jovitschitsch, *Ber.*, 1897, 30, 138. Losanitsch, 1907, 40, 4656

<sup>4</sup> Thomsen, *Zeitsch. anorg. Chem.*, 1903, 34, 187.

<sup>5</sup> Dewar and Jones, *Proc. Roy. Soc.*, 1910, A, 83, 408

unchanged below 360° C. in a vacuum, but at a low red heat a change takes place in accordance with the equation



When carbon disulphide is exposed for a long time to sunlight a red substance is obtained, which is supposed also to be a polymeric form of the monosulphide.

So far the nature of the simple substance CS had not been elucidated, but Dewar and Jones<sup>1</sup> followed up this communication with another in which evidence was forthcoming of the formation of the non-polymerised monosulphide. Carbon disulphide vapour at low pressure was submitted to the action of the silent electric discharge, with the consequence that sulphur separated. When the resulting vapour was cooled in a tube immersed in liquid air and then brought again to the temperature of the atmosphere an explosion took place, and the brown substance previously identified as  $(\text{CS})_x$  was formed. It appears, therefore, that carbon monosulphide is an endothermic gas, condensible by means of liquid air, which rapidly polymerises to  $(\text{CS})_x$  at atmospheric temperature.

**Carbon Subsulphide,  $\text{C}_3\text{S}_2$ .**—By passing the vapour of carbon disulphide over an electric arc with carbon poles, Langyel<sup>2</sup> obtained a deep red, tear-exiting liquid which appeared to be  $\text{C}_3\text{S}_2$ . When heated under reduced pressure this liquid partly distilled, and was partly converted into a black, solid polymer. With bromine it formed  $\text{C}_3\text{S}_2\text{Br}_6$ , a yellow solid with an aromatic smell.

Carbon subsulphide has more recently been obtained by Stock and Praetorius,<sup>3</sup> who found that the best way to prepare it was to strike an arc between a carbon cathode and an anode consisting of antimony containing 7 per cent. of carbon placed beneath the surface of liquid carbon disulphide. The subsulphide dissolves in the disulphide as it is formed, producing a red solution, and when separated and distilled in a vacuum and condensed in a receiver at  $-10^\circ\text{C}$ . forms a yellowish-red solid whose melting-point is  $-0.5^\circ\text{C}$ . At ordinary temperature it is a bright red, strongly refractive liquid; it has a vapour density and a molecular weight in carbon disulphide solution corresponding to the formula  $\text{C}_3\text{S}_2$ , and polymerises at  $90^\circ\text{C}$ . With aniline it forms thiomalonanilide; it therefore bears the same relation to thiomalononic acid that carbon suboxide bears to malonic acid; consequently the constitutional formula  $\text{S}-\text{C}\equiv\text{C}-\text{C}-\text{S}$  is attributed to this compound.

**Carbon Sulphidoselenide,  $\text{CSSe}$ ,** was obtained by Stock and Willfroth<sup>4</sup> by striking an electric arc under carbon disulphide between a graphite cathode and an anode containing 17.5 parts of graphite to 100 of selenium. It is an intensely yellow liquid smelling of onions; its density is 1.979, melting-point  $-85^\circ\text{C}$ ., boiling-point  $84^\circ\text{C}$ ., and  $\mu_D^{20}$  1.7349. It is decomposed by light, or on long keeping at atmospheric temperature. With alcoholic sodium ethoxide it forms sodium monoselenoxanthate,  $\text{SeC}(\text{SNa})(\text{OC}_2\text{H}_5)$ .

<sup>1</sup> Dewar and Jones, *Proc. Roy. Soc.*, 1910, **A**, 83, 526.

<sup>2</sup> Langyel, *Ber.*, 1893, 26, 2960.

<sup>3</sup> Stock and Praetorius, *Ber.*, 1912, 45, 3768.

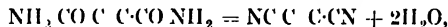
<sup>4</sup> Stock and Willfroth, *Ber.*, 1911, 47, 144.

**Carbon Sulphidotelluride, CSt<sub>2</sub>**, was prepared by Stock and Praetorius<sup>1</sup> in the same way as the previous compound, the anode consisting of 10 or more parts of graphite to 100 of tellurium. Owing to the instability of this substance, its preparation was carried out in a weak light, and below  $-30^{\circ}\text{C}$ .; it formed yellowish-red crystals melting at  $-54^{\circ}\text{C}$ . to a brilliant red liquid with a garbe-like odour whose density at  $-50^{\circ}\text{C}$ . was 2.9. Molecular weight determinations with benzene and carbon disulphide as solvents gave values between 176 and 181, theory for CSt<sub>2</sub> requiring 172. When kept for a short time at atmospheric temperature carbon sulphidotelluride decomposed completely. The supposed carbon telluride, CTe<sub>2</sub>, previously described<sup>2</sup> could not be obtained; the phenomena recorded were due to the decomposition of the sulphidotelluride.

#### CARBON AND NITROGEN

**Carbon Nitrides.**—Besides cyanogen, to be described below, carbon is known to form two other nitrides, C<sub>3</sub>N<sub>2</sub> and C<sub>6</sub>N<sub>2</sub>, which have recently been obtained from organic sources.<sup>3</sup>

**Carbon Subnitride, C<sub>3</sub>N<sub>2</sub>**, is dicyanaethylene, NC≡C≡CN, and the nitrile of acetylene dicarboxylic acid; it is formed by the elimination of two molecules of water from the amide of that acid:



is crystalline, melts at  $20.5^{\circ}\text{--}21^{\circ}\text{C}$ ., and boils at  $76^{\circ}\text{C}$ . under 753 mm. pressure.

Another subnitride, C<sub>6</sub>N<sub>2</sub>, is probably the nitrile of diacetylene dicarboxylic acid, and thus has the constitution NC≡C≡C≡C≡C≡CN. It is prepared by oxidising cyanaethylene, CH<sub>2</sub>:C≡CN, with potassium ferri-cyanide, and forms crystalline needles melting at  $64^{\circ}\text{C}$ .

#### CYANOGEN, HYDROCYANIC ACID, AND THE CYANIDES

**History.** Prussian blue, which is ferric ferrocyanide, was discovered by Diesbach early in the eighteenth century. Dippel, Woodward, John Brown, and Geoffroy studied the conditions under which this substance is formed, and Macquer, in 1752, showed that when it is boiled with potash, oxide of iron separates, and the body known later as prussiate of potash remains in solution. Scheele investigated this latter compound in 1782-5, and obtained prussic acid, *i.e.* hydrocyanic acid, by distilling it with sulphuric acid. In 1787 Berthollet proved that prussiate of potash contains iron, alkali, and prussic acid, and that the last-named substance consists of carbon, nitrogen, and hydrogen. Gay Lussac, in 1811, showed that prussic acid consists of hydrogen united to the "compound radicle" cyanogen (κύανος, dark blue, γέννω, I produce) and in 1815 prepared cyanogen itself.

<sup>1</sup> Stock and Praetorius, *Ber.*, 1914, 47, 131.

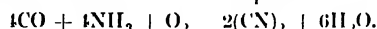
<sup>2</sup> Stock and Blumenthal, *Ber.*, 1911, 44, 1832.

<sup>3</sup> Moureu and Bougrand, *Compt. rend.*, 1910, 150, 225, 151, 946.

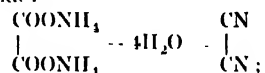
CYANOGEN (*Dicyanogen*)Formula,  $(\text{CN})_2$ 

Cyanogen gas is an endothermic compound which is formed by the union of its elements at very high temperature. According to von Wautenberg<sup>1</sup> 44 per cent. of cyanogen should be produced when carbon and nitrogen are in equilibrium at 3500° C., the temperature of the electric arc. The presence of this gas in the arc is shown by its spectrum,<sup>2</sup> but Wallis<sup>3</sup> failed to find it in the gases withdrawn from the arc chamber. This may be due to the catalytic decomposition of cyanogen by carbon particles, or by its union with hydrogen from the arc carbons to form HCN.

Cyanogen is formed in small quantity in the gases from coke-ovens and blast-furnaces<sup>4</sup>; and also when a mixture of coal gas and ammonia is burnt in a Bunsen burner, the reaction probably being:

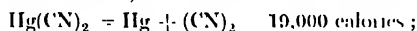


It may also be obtained by dehydrating ammonium oxalate by heating it with phosphoric oxide:

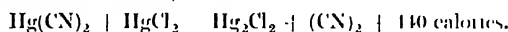


but is most conveniently prepared by heating certain metallic cyanides. Metals whose oxides yield metal and oxygen when heated, *i.e.* mercury, silver, and gold, are those whose cyanides give in the same way metal and cyanogen. In addition to these, cupric cyanide very readily decomposes like cupric iodide, yielding cuprous cyanide and cyanogen.

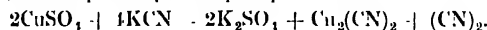
Cyanogen is frequently prepared by heating powdered mercuric cyanide in a hard glass tube, and is collected over mercury. Much heat is needed for this reaction, as is shown by the thermal equation<sup>5</sup>:



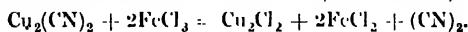
admixture of mercuric chloride, however, enables the reaction to proceed at a lower temperature, owing to the formation of mercurous chloride by an exothermic reaction, thus:



A mixture of potassium ferrocyanide and mercuric chloride also when heated yields cyanogen, probably mixed with nitrogen. The most convenient way, however, of obtaining cyanogen is by warming together potassium cyanide and cupric sulphate solutions. Cyanogen is evolved, and cuprous cyanide precipitated:



If the cuprous cyanide is filtered, washed, and treated with ferric chloride solution the remainder of the cyanogen is evolved,<sup>6</sup> thus:



<sup>1</sup> Von Wautenberg, *Zeitsch. anorg. Chem.*, 1907, 52, 299.

<sup>2</sup> Fowler and Shaw, *Proc. Roy. Soc.*, 1912, A, 86, 118.

<sup>3</sup> Wallis, *Annalen*, 1906, 345, 373.

<sup>4</sup> Bunsen and Playfair, *J. prakt. Chem.*, 1847, 42, 145.

<sup>5</sup> Thomson, *Thermochemische Untersuchungen*, 1886, vol. iv, 390.

<sup>6</sup> Jacquemin, *Ann. Chim. Phys.*, 1886, [vi], 6, 140.



**Physical Properties.**—Cyanogen is a colourless, poisonous gas with an odour resembling that of peach kernels. Its density is 1.8064 (Gay Lussac), the theoretical density being 1.7993. The gas shows no sign of dissociation at 800° C.; but is liquefied at  $-20.7^{\circ}$  C. under 1 atm. The vapour pressures at different temperatures are as follow <sup>2</sup>:

Temperature ° C.	$-20.7^{\circ}$	$0^{\circ}$	$5^{\circ}$	$10^{\circ}$	$15^{\circ}$
Vapour pressure (atm.)	1.0	2.37	2.83	3.38	4.04

The density of liquid cyanogen <sup>3</sup> at  $17.2^{\circ}$  C. is 0.866; according to Dewar its critical temperature is  $124^{\circ}$  C. and critical pressure 61.7 atm. <sup>4</sup> whence the constants for van der Waals' equation are derived:  $a = 0.01416$ ;  $b = 0.0029$ . Cardoso and Baume, <sup>5</sup> however, give: critical temperature  $128.3^{\circ}$  C., critical pressure 59.6 atm. When cooled below  $-35^{\circ}$  C. liquid cyanogen freezes to a crystalline mass which melts at  $-34.4^{\circ}$  C. <sup>6</sup>

The heat of formation of cyanogen from graphite and nitrogen is  $-73,000$  to  $-70,000$  calories; its molecular heat of combustion to  $\text{CO}_2$  and  $\text{N}_2$  is 262,500 calories (Berthelot <sup>7</sup>) or 259,600 calories (Thomsen <sup>8</sup>).

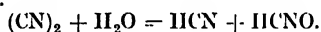
Water, at atmospheric temperature, dissolves about four and a half times its volume of cyanogen gas, alcohol about twenty-three times its volume. Water, however, acts chemically on cyanogen, causing the separation of a brown insoluble substance known as azulinic acid, and

at the same time hydrolysing the cyanogen  $\left( \begin{smallmatrix} \text{CN} \\ | \\ \text{CN} \end{smallmatrix} \right)$ , producing from it

oxamide  $\left( \begin{smallmatrix} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{smallmatrix} \right)$ , oxamic acid  $\left( \begin{smallmatrix} \text{CONH}_2 \\ | \\ \text{COOH} \end{smallmatrix} \right)$ , oxalic acid  $\left( \begin{smallmatrix} \text{COOH} \\ | \\ \text{COOH} \end{smallmatrix} \right)$ ,

and their ammonium salts; together with the following compounds containing only one carbon atom: hydrocyanic acid, urea  $\left( \begin{smallmatrix} \text{NH}_2 \\ \diagup \text{CO} \diagdown \\ \text{NH}_2 \end{smallmatrix} \right)$ ,

and ammonium carbonate. When cyanogen is passed into water at  $0^{\circ}$  C., however, the reaction is simple, hydrocyanic and cyanic acids being formed thus:



This reaction has been studied <sup>9</sup> by measuring the conductivity due to hydrocyanic acid, cyanic acid being almost a non-conductor.

**Chemical Properties.**—The chemical constitution of cyanogen,  $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$ , follows from the reactions which this gas undergoes. Thus it is reduced by tin and hydrochloric acid to ethylene diamine, which is  $\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ , and is hydrolysed by water and dilute acids as follows:

<sup>1</sup> V. Meyer and Goldschmidt, *Ber.*, 1882, 15, 1161.

<sup>2</sup> Chappuis and Rivière, *Compt. rend.*, 1887, 104, 1501.

<sup>3</sup> Faraday, *Phil. Trans.*, 1845, 135, 1, 155.

<sup>4</sup> Dewar, *Phil. Mag.*, 1885, [v], 18, 210.

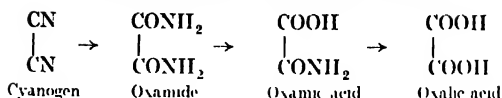
<sup>5</sup> Cardoso and Baume, *Compt. rend.*, 1910, 151, 141.

<sup>6</sup> Davy and Faraday, *Phil. Trans.*, 1823, 11, 196.

<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1889, [vi], 18, 127.

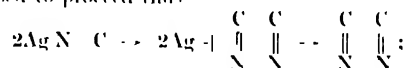
<sup>8</sup> Thomsen, *Thermochemische Untersuchungen*, 1882, vol. II, 387.

<sup>9</sup> Naumann, *Zeitsch. Elektrochem.*, 1910, 16, 772.

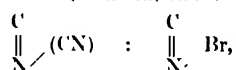


Cyanogen is thus the nitrile of oxalic acid.

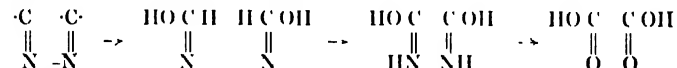
Dixon and Taylor,<sup>1</sup> however, favour a cyclic constitution for cyanogen:  $\begin{array}{c} \text{C} \quad \text{C} \\ || \quad || \\ \text{N} - \text{N} \end{array}$ , partly on account of its preparation by heating silver and mercuric cyanides, which are probably *iso*-compounds, the reaction being supposed to proceed thus:



and also on account of its reaction with alkalis being similar to that of cyanogen bromide, which suggests that one cyanogen group behaves towards the other like a halogen atom, thus:



the formula for cyanogen bromide being that of Gutmann.<sup>2</sup> Dixon and Taylor suggest that if cyanogen has an *iso*-constitution oxalic acid might be derived from it, thus:



There is a polymeric modification of cyanogen known as *paracyanogen*  $(\text{CN})_n$ . It is a brown powder of unknown molecular weight and constitution, whose formation is observed when mercuric cyanide is heated. It is produced when cyanogen is heated for some time at  $110^\circ \text{C}$ ., and is formed at the anode during the electrolysis of potassium cyanide solution.<sup>3</sup> Cyanogen is converted into paracyanogen under ordinary pressure at about  $310^\circ \text{C}$ ., and under 300 atmospheres pressure at  $220^\circ \text{C}$ .<sup>4</sup> Paracyanogen yields ordinary cyanogen gas, which condenses to liquid cyanogen. The two forms are thus monotropic like white and red phosphorus.<sup>5</sup> Paracyanogen is insoluble in water and alcohol; it shows, however, many of the reactions of cyanogen, although its reactivity is slow.

Cyanogen is decomposed into its elements by being passed through a red-hot tube, or by the agency of electric sparks or the arc flame.<sup>6</sup> It burns with a characteristic peach-coloured flame, which consists of a red internal and a blue external zone separable by means of Smithells' apparatus. In the inner flame the reaction  $(\text{CN})_2 + \text{O}_2 = 2\text{CO} + \text{N}_2$  takes place; in the outer flame CO burns<sup>7</sup> to  $\text{CO}_2$ .

<sup>1</sup> Dixon and Taylor, *Trans. Chem. Soc.*, 1913, 103, 980.

<sup>2</sup> Gutmann, *Ber.*, 1909, 42, 3623.

<sup>3</sup> Hittorf, *Zeitsch. physikal. Chem.*, 1892, 10, 616.

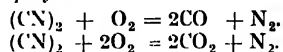
<sup>4</sup> Bruner and Wroczynski, *Compt. rend.*, 1910, 151, 311.

<sup>5</sup> Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 27.\*.

<sup>6</sup> Schutzenberger, *Compt. rend.*, 1890, 111, 774; Berthelot, *Compt. rend.*, 1887, 95, 955.

<sup>7</sup> Smithells, *Trans. Chem. Soc.*, 1892, 61, 204, 1894, 65, 603.

Cyanogen can burn or be exploded in dried oxygen,<sup>1</sup> one or other of the following reactions occurring in the latter case according to the volume of oxygen employed :



A mixture of dried oxygen and carbon monoxide is not explosive, but the admixture of 10 per cent. of cyanogen gas secures the explosion of the carbon monoxide in the absence of moisture.<sup>2</sup>

Whilst behaving as the nitride of oxalic acid in some of its reactions, in others cyanogen resembles free chlorine. Thus it unites with hydrogen to form hydrocyanic acid and with metals such as potassium, zinc, copper, lead, mercury, and silver to produce cyanides. Its reaction with sulphurous acid, though slower than, is similar to, that of the halogens<sup>3</sup>:  $(\text{CN})_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{HCN} + \text{H}_2\text{SO}_4$ .

Moreover, just as chlorine reacts with dilute alkali to form chloride and hypochlorite, so cyanogen yields cyanide and cyanate, thus :



**Detection and Estimation of Cyanogen.**—Cyanogen gas is easily detected by its smell, by its decomposition by electric sparks into nitrogen and carbon, and by its characteristic flame, whose spectrum contains prominent bands in the blue and violet. The presence of this gas in a mixture may be detected by its reaction with a mixture of 2 c.c. of cold saturated solution of picric acid, 18 c.c. of alcohol, and 5 c.c. of a 15 per cent. solution of caustic soda. With this solution cyanogen gives a purple-red colour turning brown, due to the formation of isopurpuric acid. If much cyanogen is present the potassium salt of this acid separates as a purple-red oil. Cyanogen may be estimated by combustion in a stream of oxygen; explosion with oxygen does not give accurate results.

#### HYDROCYANIC ACID (*Prussic Acid*)

Formula,  $\text{HCN}$

Hydrocyanic acid was discovered by Scheele in 1782 and first obtained anhydrous by Gay Lussac,<sup>4</sup> who heated mercury cyanide with hydrochloric acid, and after passing the evolved gas over marble to remove  $\text{HCl}$ , and subsequently drying, condensed the hydrocyanic acid in a freezing mixture.

This acid occurs in plants, very seldom in the free state, but generally as a constituent of the glycoside amygdalin, which on hydrolysis yields hydrocyanic acid, benzaldehyde, or bitter almond oil, and glucose, as follows :



This hydrolysis occurs naturally by the agency of the enzyme emulsin; it is brought about artificially by the action of dilute acids. Bitter almonds and laurel leaves are the chief sources of amygdalin; and

<sup>1</sup> Dixon, *Trans. Chem. Soc.*, 1886, 49, 384.

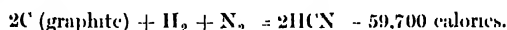
<sup>2</sup> Beketoff, *Bull. Acad. Sci. Petrograd*, 1895, [n], 2, 175.

<sup>3</sup> Vorlander, *Verh. Ges. deut. Naturforsch. Aerzte*, 1907, ii, 92.

<sup>4</sup> Gay Lussac, *Ann. Chim.*, 1811, 78, 128; and 1815, 95, 136.

by distilling these products with water a dilute solution of hydrocyanic acid is obtained.

Hydrogen cyanide has been synthesised from its elements by passing a mixture of hydrogen and air through a carbon tube heated in an electric arc.<sup>1</sup> The reaction is endothermic, and, according to von Wartenberg,<sup>2</sup> is represented by the following thermal equation:



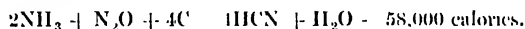
The amount of hydrogen cyanide formed increases with temperature, as theory indicates, and Wallis,<sup>3</sup> by passing a mixture of nitrogen and hydrogen across the carbon poles of the electric arc, whose temperature is about 3500° C., converted 33.6 per cent. of the gaseous mixture into hydrogen cyanide.

By means of an electric flame an even more striking result has been obtained; for by employing a mixture of nitrogen and methane in the molecular proportion of 2:3:1, diluted with hydrogen so as to contain less than 10 per cent. of methane, Muthmann and Schaidhauf<sup>4</sup> have converted the methane quantitatively into hydrogen cyanide. Lipinski<sup>5</sup> also converted the whole of the methane in a mixture of 8 to 31 per cent.  $CH_4$ , 7.5 to 53 per cent.  $N_2$ , and 16 to 12 per cent.  $H_2$  into hydrogen cyanide by the passage of an alternating current at 2000 volts and 0.05 to 0.12 ampere between platinum terminals through 3.8 litres of the mixture for one to three hours.

A less complete synthesis of hydrogen cyanide would be effected by causing ammonia, in which nitrogen and hydrogen are already united, to react with carbon, according to the equation



Bergmann<sup>6</sup> has shown that when ammonia is passed over carbon heated to about 1300° C., 90 per cent. of it is converted into HCN. The reaction is endothermic, its heat being -39,500 calories. A modification of this reaction is that of Roeder and Grunwald,<sup>7</sup> who pass a mixture of ammonia and nitrous oxide over heated carbon, the reaction being



Owing to the heat of decomposition of nitrous oxide, which is endothermic, and the heat of formation of steam, it is not necessary to heat the carbon to so high a temperature as in the former case; indeed the yield of hydrogen cyanide is nearly quantitative when the temperature of the carbon is but 150° C.

Hydrogen cyanide is also produced by the explosion of a mixture of acetylene and nitrogen in a bomb<sup>8</sup>:



<sup>1</sup> Dewar, *Chem. News*, 1879, 39, 282.

<sup>2</sup> Von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 52, 299.

<sup>3</sup> See Bergmann, *J. Gasbeleuchtung*, 1896, 117.

<sup>4</sup> Muthmann and Schaidhauf, *Zeitsch. Elektrochem.*, 1911, 17, 497.

<sup>5</sup> Lipinski, *Zeitsch. Elektrochem.*, 1911, 17, 761, but see Mosericki, *ibid.*, 1911, 17, 877;

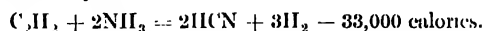
<sup>6</sup> *ibid.*, 1912, 18, 229, 730.

<sup>7</sup> Bergmann, *J. Gasbeleuchtung*, 1896, 117.

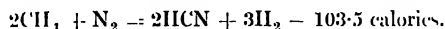
<sup>8</sup> Roeder and Grunwald, *Chem. Zentr.*, 1902, ii, 235.

<sup>9</sup> Mixer, *J. Amer. Chem. Soc.*, 1902, [iv], 10, 295.

and by the reaction between acetylene and ammonia at 300° C. in presence of a catalyst<sup>1</sup>:



Methane and nitrogen also yield hydrogen cyanide under the influence of the silent electric discharge, or at 1000° C.,<sup>2</sup> the equation being:



Hydrogen cyanide is generally prepared, however, from potassium ferrocyanide or a simple cyanide. In either case it is synthetic in origin, for ferrocyanide was originally made by heating together a mixture of potassium carbonate, iron, and nitrogenous organic matter, whilst cyanide is obtained either from the hydrogen cyanide formed synthetically in gas manufacture or by passing ammonia over a heated mixture of alkali carbonate, and carbon (Beilby's process<sup>3</sup>). When powdered potassium ferrocyanide is distilled with dilute sulphuric acid (1 part  $\text{H}_2\text{SO}_4$  to 2 parts water) hydrocyanic acid is evolved according to the reaction:



The vapour may be dried by passing it through calcium chloride tubes kept at 30° C. by immersion in warm water, and then condensed in a freezing mixture; or the vapour may be at once passed into water if only a solution of the acid is required.

Practically anhydrous hydrocyanic acid may be obtained by dropping sulphuric acid diluted with an equal volume of water on to 98 per cent. potassium cyanide.<sup>4</sup>

Anhydrous hydrocyanic acid is also formed when mercuric cyanide, heated to 30° C., is decomposed by hydrogen sulphide.

**Physical Properties.** Anhydrous hydrogen cyanide is a colourless, mobile liquid having a smell of bitter almonds, and is exceedingly poisonous. Owing to the danger of working with this substance its physical properties have not been completely elucidated. Its density at 18° C. is 0.6969, and at 7° C. is 0.7058,<sup>5</sup> whence the density at 0° C. has been calculated to be 0.7115<sup>6</sup>, its boiling-point at atmospheric pressure is 26.5° C. (Gay Lussac); its vapour density at high temperature is 0.947 (air = 1) and 13.69 (H = 1); at -15° C. it solidifies to a mass of white feathery crystals.

The heat of vaporisation of hydrogen cyanide is 210.7 calories per gram, or 5700 calories per gram molecule<sup>7</sup>; this value is high on account of polymerisation. Rapid evaporation causes a drop of the liquid on a glass rod to solidify.

The following thermal values have been determined by Berthelot<sup>8</sup> and Thomsen<sup>9</sup>:

<sup>1</sup> Hoyermann, *Chem. Zeit.*, 1902, 26, 70.

<sup>2</sup> Gow, *Electroch. Met. Ind.*, 1903, 3, 472.

<sup>3</sup> See "Advances in Chemical Industry during the Nineteenth Century," *Proc. Roy. Phil. Soc.*, Glasgow, 1904.

<sup>4</sup> Wade and Panton, *Trans. Chem. Soc.*, 1898, 73, 255.

<sup>5</sup> Gay Lussac, *Ann. Chim. Phys.*, 1815, 95, 136.

<sup>6</sup> Centnerszwer, *Zeitsch. physikal. Chem.*, 1901, 39, 217.

<sup>7</sup> Berthelot, *Compt. rend.*, 1874, 78, 716; Thomsen, *Ber.*, 1880, 13, 1392.

<sup>8</sup> Berthelot, *Ann. Chim. Phys.*, 1875, [vi], 5, 431; 1881, 23, 253.

<sup>9</sup> Thomsen, *Thermochemische Untersuchungen*, 1882, vol. ii, 389.

Heat of formation HCN vapour	— 30,500 calories	
" " liquid	-- 24,800	Berthelot.
" " in solution	-- 24,100	"
" " from diamond	- 30,200	"
" " from graphite	- 29,850	Thomsen.

The heat of combustion at constant pressure is 159,300 calories (Berthelot) or 158,600 calories (Thomsen); the heat of aqueous solution is 400 calories (Berthelot).

Liquid hydrogen cyanide dissolves many organic and inorganic substances. Interesting results relating to the electric conductivity and chemical reactivity of such solutions have been obtained by Kahlenberg and Schlundt.<sup>1</sup>

Hydrogen cyanide mixes in all proportions with water, alcohol, and ether. Solution in these cases is accompanied both by fall of temperature and diminution of volume. No definite hydrate of hydrogen cyanide is known.

**Chemical Properties.** Hydrogen cyanide vapour burns with a violet flame of slight luminosity; both the anhydrous liquid and its concentrated aqueous solution appear combustible. When passed over heated copper oxide the vapour burns to carbon dioxide, water, and nitrogen.

A polymer of hydrogen cyanide is slowly produced when an aqueous solution of the latter is kept in presence of alkali carbonate or cyanide. Under these conditions the liquid turns brown, and a black mass separates after some days, from which ether extracts a substance which crystallises in colourless leaflets. This substance possesses the composition  $(\text{HCN})_n$ , turns brown at 110°C with partial decomposition, and melts at 180°C. It is decomposed by being heated with baryta water into carbonic acid, ammonia, and amino-acetic acid; it is there-

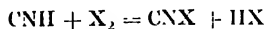
fore probably the dinitrile of aminomalonic acid,  $\text{NH}_2\text{CH} \begin{smallmatrix} \text{CN} \\ \diagup \\ \text{CN} \end{smallmatrix}$ .

That hydrogen cyanide is itself the nitrile of formic acid is shown by the fact that it is resolved into this acid and ammonia when boiled with concentrated mineral acids and alkalis:

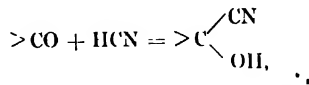


Hydrogen cyanide is reduced to methylamine,  $\text{CH}_3\text{NH}_2$ , by nascent hydrogen or by hydrogen gas at 110°C in presence of platinum black.

In sunlight chlorine converts hydrogen cyanide into cyanogen chloride; cyanogen bromide and iodide are also produced, though less readily, from hydrogen cyanide and the corresponding halogen according to the equation:

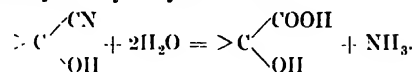


Hydrogen cyanide reacts with an organic carbonyl group, producing a cyanhydrin, thus:



<sup>1</sup> Kahlenberg and Schlundt, *J. Physical Chem.*, 1901, 5, 157

whence by hydrolysis a hydroxyacid results :



An aqueous solution of hydrogen cyanide is a very weak acid : hydrocyanic or prussic acid.

A solution of the acid does not redden litmus : its soluble salts are largely hydrolysed in aqueous solution, and are decomposed by atmospheric carbon dioxide, so that they smell of hydrocyanic acid.

The electric conductivity of aqueous hydrocyanic acid has been measured by Walker and Cornack <sup>1</sup> at 18° C., with the following results :

$v$	$\lambda_p$	$\gamma$	$K$
2	0.0183	$5.12 \times 10^{-5}$	0.00131
4	0.0262	$7.38 \times 10^{-5}$	0.00133
8	0.0320	$8.94 \times 10^{-5}$	0.00133
16	0.0365	$10.19 \times 10^{-5}$	0.00130
		Mean .	0.00132

The dissociation constant, which may be taken to be  $1.3 \times 10^{-4}$ , shows the strength of hydrocyanic acid to be only one-fortieth that of hydrogen sulphide and one two-hundredth that of carbonic acid. From measurements of the hydrolysis of potassium cyanide at 25° C. van Laar <sup>2</sup> has found the value  $K = 3.1 \times 10^{-8}$ , whilst by measuring the potential between a silver electrode and a solution of potassium silver cyanide at 18°C. Morgan <sup>3</sup> found  $K = 2.6 \times 10^{-8}$ . The percentage degree of electrolytic dissociation of hydrocyanic acid in decinormal solution <sup>4</sup> is 0.011.

The catalytic influence of the cyanide ion in promoting the change of benzaldehyde into benzoin has been studied by Stern, <sup>5</sup> and the mechanism of the addition of the elements of HCN to carbon compounds by Lapworth. <sup>6</sup>

**The Cyanides.**—The cyanides of the alkali and alkaline earth metals are soluble in water and are considerably ionised in solution. Other cyanides except mercuric cyanide are insoluble. Because of the weakness of hydrocyanic acid, mercuric cyanide shows, to a greater degree than other mercuric salts, chemical inertness in solution owing to feeble ionisation. Silver cyanide resembles silver chloride in physical properties; it is a white, curdy precipitate, which, however, differs from the chloride by its solubility in concentrated nitric acid. The

<sup>1</sup> Walker and Cornack, *Trans. Chem. Soc.* 1900, 77, 16. See this volume, p. 130. where  $v$ ,  $\lambda_p$ ,  $\gamma$ , and  $K$  are defined.

<sup>2</sup> Van Laar, *Zeitsch. physikal. Chem.*, 1893, 12, 745.

<sup>3</sup> Morgan, *Zeitsch. physikal. Chem.*, 1895, 17, 534.

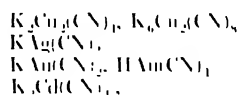
<sup>4</sup> Walker and Cornack, *Trans. Chem. Soc.*, 1900, 77, 16. See this volume, p. 130.

<sup>5</sup> Stern, *Zeitsch. physikal. Chem.*, 1905, 50, 513.

<sup>6</sup> Lapworth, *Trans. Chem. Soc.*, 1903, 83, 995, and 1904, 85, 1206.

solubility of silver cyanide in potassium cyanide solution with the formation of  $\text{KAg(CN)}_2$ , containing the anion  $\text{Ag(CN)}_2^-$  illustrates an important general property of the cyanides, that of forming complex cyanides. These are of different degrees of stability from the least stable, as for instance  $\text{K}_2\text{Ni(CN)}_4$ , dilute mineral acids reprecipitate the simple insoluble cyanide from the most stable, as for instance  $\text{K}_4\text{Fe(CN)}_6$ , the free, solid acid, e.g.  $\text{H}_4\text{Fe(CN)}_6$  is separated by mineral acid. The following list includes representatives of the complex cyanides, which, like the ammonies, are formed by the members of the eighth and contiguous groups. These compounds will be dealt with in detail under the respective metals.

Copper, silver, gold, and cadmium form the following complex cyanides:



whilst chromium, manganese, and the metals of the eighth group form complex cyanides of several different types, as the following table shows. Where the free acid is known its formula appears.

	$\text{H}_2\text{M(CN)}_4$	$\text{H}_4\text{M(CN)}_6$	$\text{H}_6\text{M(CN)}_6$
Cu . . . . .		$\text{H}_2\text{Cu(CN)}_4$	$\text{K}_4\text{Cu(CN)}_6$
Mn . . . . .		$\text{H}_2\text{Mn(CN)}_6$	$\text{K}_4\text{Mn(CN)}_6$
Fe . . . . .		$\text{H}_2\text{Fe(CN)}_6$	$\text{H}_4\text{Fe(CN)}_6$
Ni . . . . .	$\text{K}_2\text{Ni(CN)}_4$		
Co . . . . .		$\text{H}_2\text{Co(CN)}_6$	$\text{H}_4\text{Co(CN)}_6$
Ru . . . . .		$\text{H}_2\text{Ru(CN)}_6$	
Rh . . . . .			$\text{K}_3\text{Rh(CN)}_6$
Pd . . . . .	$\text{K}_2\text{Pd(CN)}_4$		
Os . . . . .		$\text{H}_2\text{Os(CN)}_6$	
Ir . . . . .		$\text{K}_3\text{Ir(CN)}_6$	$\text{H}_4\text{Ir(CN)}_6$
Pt . . . . .	$\text{H}_2\text{Pt(CN)}_4$		

**Constitution of Hydrocyanic Acid, Cyanogen Halides, and the Cyanides.** Hydrogen cyanide, cyanogen halide, and a metallic cyanide may be formulated respectively as



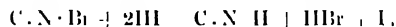
The normal formulae, first given, have generally been preferred, because they show the carbon atom to be quadrivalent, whilst the nitrogen atom is trivalent, but there is a reason<sup>1</sup> for preferring the *iso* formulae, in which hydrogen, halogen, or metal is attached to nitrogen rather than to carbon.

The reactivity of halogen and hydrogen atoms attached to nitrogen is superior to the reactivity of the same atoms attached to carbon;

<sup>1</sup> Chattaway and Wadmore, *Trans. Chem. Soc.*, 1902, 81, 191, see also Michael and Hibbert, *Annalen*, 1909, 364, 61.



and a study of the cyanogen halides shows them to possess all the characteristics of compounds having halogen attached to nitrogen. This is borne out by such a reaction as the following



which, being easy of achievement, is regarded as proving that bromine is attached to nitrogen.

Now the cyanogen halides are readily formed from hydrocyanic acid and its salts, which therefore in all probability have a similar composition, being *iso* compounds, thus :



*Additive Compounds of Hydrogen Cyanide*.—When hydrogen chloride is passed into anhydrous hydrogen cyanide at  $-10^\circ\text{C}$ ., and the solution is then heated to  $35^\circ\text{C}$ ., the compound  $\text{HCN} \cdot \text{HCl}$  is formed,<sup>1</sup> and crystallises on cooling. If hydrogen cyanide has the constitution  $\text{C:N} \cdot \text{H}$ , the

compound with  $\text{HCl}$  is  $\text{C} \begin{smallmatrix} \text{N} \cdot \text{H} \\ \text{Cl} \end{smallmatrix}$ . This compound is very hygroscopic

and is decomposed by water into formic acid and ammonium chloride, but may be sublimed. Another compound,  $2\text{HCN} \cdot 3\text{HCl}$ ,<sup>2</sup> exists which appears to be the hydrochloride of dichloromethylformamidine,<sup>3</sup>  $(\text{NH}=\text{CH}-\text{NH}-\text{CHCl}_2) \cdot \text{HCl}$ .

**Physiological Action of Hydrocyanic Acid.** Hydrocyanic acid is one of the most powerful poisons known, and it is very rapid in its action. An amount equal to  $\frac{1}{100,000}$ th part of the weight of its blood suffices to kill a dog,<sup>4</sup> and a few drops brought into a dog's eye kills the animal in thirty seconds; 0.05 gram has proved a fatal dose for a man, though larger quantities have been taken without fatal effects. The symptoms of poisoning by prussic acid are headache, nausea, difficulty of breathing, palpitations, tetanic spasms affecting the muscles of the jaws and limbs, paralysis, and insensibility.

The cause of the poisonous action of hydrocyanic acid and the soluble cyanides is not known, but an analogy has been traced between this action and the inhibiting effect of the same substance on catalysts such as ferments and colloidal metals.<sup>5</sup>

Ammonia or chlorine water appears to serve as an antidote, though in neither case is the chemical action understood.

**Detection and Estimation.**—In cases of poisoning hydrocyanic acid is separated from the matter containing it by distillation with tartaric acid. For the detection of small quantities of hydrocyanic acid in aqueous solution several methods are available.

(1) The cyanide may be converted into Prussian blue by boiling its solution with alkali with the addition of ferrous and ferric salt. On acidifying ferric ferrocyanide separates as a deep blue precipitate, or, if only a trace of cyanide was present, shows a blue or green colour. By this test 1 part of cyanide in 50,000 can be detected. Extremely dilute solutions of hydrogen cyanide containing as little as 0.00002

<sup>1</sup> Gautier, *Ann. Chim. Phys.*, 1869, [iv], 17, 103.

<sup>2</sup> Clausen and Matthews, *Trans. Chem. Soc.*, 1882, 41, 284.

<sup>3</sup> Gattermann and Schultze, *Ber.*, 1898, 31, 1770.

<sup>4</sup> Girchant, *Compt. rend.*, 1889, 109, 502.

<sup>5</sup> Schonlem, *Exper. Chem.*, 1863, 89, 334. Brechig, *Zeitsch. physikal. Chem.*, 1899, 31, 258; Senter, *Zeitsch. physikal. Chem.*, 1903, 44, 257; 1905, 51, 673.

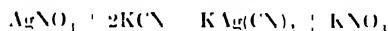
gram per c.c. may be made alkaline, evaporated to small bulk, and then tested for in this way.<sup>1</sup>

(ii) Conversion into nitroprusside,<sup>2</sup> which gives a purple colour with alkali sulphide, serves to detect 1 part of cyanide in 300,000.

(iii) By evaporation to dryness with yellow ammonium sulphide cyanide is converted into thiocyanate, which gives a blood-red colour with ferric chloride.<sup>3</sup> This test will detect 1 part of cyanide in even 4,000,000 parts of solution.

(iv) Cyanide solution gives a deep red colour<sup>4</sup> with picric acid.

Cyanide is estimated volumetrically by adding to its alkaline solution standard silver nitrate solution until a permanent precipitate appears. One molecule of silver nitrate then corresponds to two molecules of cyanide owing to the formation of  $\text{KAg}(\text{CN})_2$ , according to the reaction:



The estimation may be carried out gravimetrically by weighing the corresponding silver cyanide, or by reducing it and weighing the metallic silver.

#### HALOGEN DERIVATIVES OF HYDROCYANIC ACID

The hydrogen atom in the molecule of hydrocyanic acid is replaceable by a halogen atom forming  $\text{CNCl}$ ,  $\text{CNBr}$ , or  $\text{CNI}$ . These halides can polymerise, forming the cyanine halides  $(\text{CNCl})_n$ ,  $(\text{CNBr})_n$ , and  $(\text{CNI})_n$ .

**Cyanogen Chloride** (*Chlorocyanogen*)  $\text{CNCl}$ . Cyanogen chloride was first obtained by Berthollet by the action of chlorine on hydrocyanic acid. Wohler<sup>5</sup> prepared it by passing chlorine into a saturated solution of mercuric chloride and subsequently distilling; and Gautier<sup>6</sup> saturated aqueous hydrocyanic acid ( $\text{HCN}$  1Aq) with chlorine, added excess of mercuric oxide and calcium chloride to the well-cooled solution, and afterwards distilled off the cyanogen chloride. Hantzsch and Mai<sup>7</sup> added potassium cyanide to saturated chlorine water at 0° C. till all the chlorine was absorbed, then again saturated the liquid with chlorine and added more cyanide. The cyanogen chloride thus formed was then vapourised and condensed.

Cyanogen chloride has been variously described as a gas and a liquid. Possibly two forms of the liquid exist which boil at  $-12^\circ \text{C}$ . and  $+12.7^\circ \text{C}$ . (Regnault<sup>8</sup>) or  $15.5^\circ \text{C}$ . (Wurtz<sup>9</sup>) respectively. The vapour density is in either case 2.13 which corresponds to the molecular formula  $\text{CNCl}$ . The vapour has an irritating smell.

Liquid cyanogen chloride solidifies at  $-18^\circ \text{C}$ . (Regnault) to a mass of long, transparent prisms which melt at  $-7.7^\circ \text{C}$ . or, according to Wurtz, at  $-12^\circ \text{C}$ . to  $-15^\circ \text{C}$ .

The heat of formation of cyanogen chloride is -426,900 calories,

<sup>1</sup> Landolt and Waden, *Indust.* 1911, 39, 266.

<sup>2</sup> Vorlmann, *Ber. Monatsh.* 1886, 7, 116.

<sup>3</sup> Liebig, *Annalen*, 1851, 77, 102.

<sup>4</sup> Brann, *Zeitsch. anal. Chem.* 1864, 3, 461.

<sup>5</sup> Wohler, *Annalen*, 1850, 73, 219.

<sup>6</sup> Gautier, *Annalen*, 1867, 141, 122.

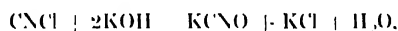
<sup>7</sup> Hantzsch and Mai, *Ber.*, 1895, 28, 2471.

<sup>8</sup> Regnault, *Jahresber.*, 1863, 65, 70, 71.

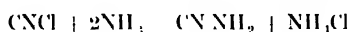
<sup>9</sup> Wurtz, *Compt. rend.* 1847, 24, 136.

and its heat of combustion 126,000 calories.<sup>1</sup> This compound dissolves in water without decomposition, also in various organic solvents.

In the pure state cyanogen chloride is stable, though under certain conditions it polymerises into cyanine chloride  $(\text{CNCl})_4$ . Alkalis decompose it into a mixture of cyanate and chloride.<sup>2</sup>



and ammonia solution forms cyanamide and ammonium chloride



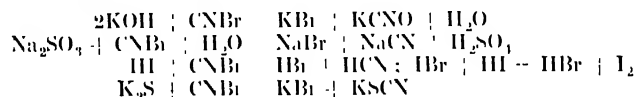
Cyanogen chloride forms the additive compounds  $\text{BCl}_2\text{CNCl}$ <sup>3</sup> and  $\text{TiCl}_4\text{CNCl}$ <sup>4</sup>, it is a synthetic agent in organic chemistry.

**Cyanogen Bromide** (*Bromocyanogen*),  $\text{CNBr}$ , resembles  $\text{CNCl}$  in its manner of preparation, being formed by the action of bromine on hydrocyanic acid or a cyanide.<sup>5</sup> It forms transparent prisms by sublimation, which pass into a cubical form; it melts at  $52^\circ\text{C}$ , and boils at  $61.3^\circ\text{C}$ <sup>6</sup>; its vapour density is 3.607, it is poisonous, and its vapour is pungent and affects the eyes. The heat of formation of  $\text{CNBr}$  from its elements is 37,000 calories, and from  $(\text{CN})_2$  and  $\text{Br}_2$  10,000 calories.<sup>6</sup> It easily polymerises to  $(\text{CNBr})_4$ .

In dilute aqueous solution cyanogen bromide shows no evidence of ionisation. Hydrogen sulphide reacts quantitatively with it, thus:



and the following reactions are also characteristic



A theory of the mechanism of these reactions is given by Dixon and Taylor.<sup>7</sup>

**Cyanogen Iodide** (*Iodocyanogen*),  $\text{CNI}$ .—This compound is formed by the action of iodine on mercuric cyanide<sup>8</sup>, if the iodine is dissolved in anhydrous ether<sup>9</sup> the cyanogen iodide goes into solution in the ether, and remains behind after the evaporation of the latter.

Iodide of cyanogen crystallises in long white needles which melt at  $116.5^\circ\text{C}$  and easily sublime, giving a vapour whose density corresponds to the formula  $\text{CNI}$ , has an unpleasant smell like that of the bromide, and is very poisonous. This compound often occurs as an impurity in commercial iodine. Its heat of formation from its elements is 23,100 calories, and from  $(\text{CN})_2$  and  $\text{I}_2$  17,900 calories.<sup>10</sup> It is easily soluble in alcohol and ether, sparingly so in water. This com-

<sup>1</sup> Lemoult, *Ann. Chim. Phys.*, 1899, [vi], 16, 338.

<sup>2</sup> Martins, *Annalen*, 1859, 109, 79.

<sup>3</sup> Wohler, *Annalen*, 1850, 73, 219.

<sup>4</sup> Serullas, *Ann. Chim. Phys.*, 1827, 34, 100; Langlois, *Ann. Chim. Phys.*, 1861, [iii], 61, 182.

<sup>5</sup> Mulder, *Re. Trav. chim.*, 1886, 4, 151–5, 85.

<sup>6</sup> Berthelot, *Compt. rend.*, 1871, 73, 448; *Ann. Chim. Phys.*, 1875, [iii], 5, 433.

<sup>7</sup> Dixon and Taylor, *Trans. Chem. Soc.*, 1913, 103, 974.

<sup>8</sup> Dax, *Gillb. Annalen*, 1816, 54, 381; Seubert and Pollard, *Ber.*, 1890, 23, 1062.

<sup>9</sup> Linnemann, *Annalen*, 1861, 120, 36.

<sup>10</sup> Berthelot, *Compt. rend.*, 1871, 73, 448; *Ann. Chim. Phys.*, 1875, [iii], 5, 433.

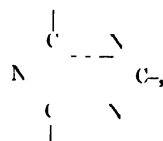
compound is unchanged in aqueous solution by hydrochloric or sulphuric acid, but reacts with hydroiodic acid thus<sup>1</sup>



The reaction between cyanogen iodide and a soluble iodide in aqueous solution is brought about by the presence of hydrogen ions. It has therefore been proposed to use it as a method of acidimetry.<sup>2</sup>

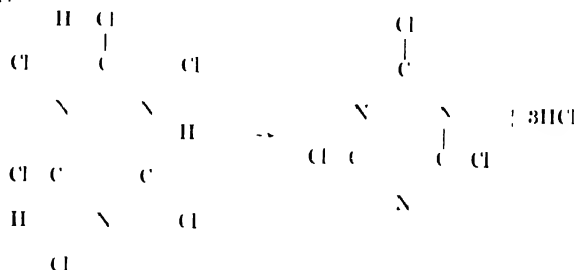
**Polymerised Cyanogen Halides.** Cyanuric chloride,  $(\text{CNCl})_3$ , cyanuric bromide,  $(\text{CNBr})_3$ , and cyanuric iodide,  $(\text{CNI})_3$ , are known.

The two former substances contain the six-membered ring—



being halides of cyanuric acid  $(\text{CNOH})_3$ , which has a similar constitution. Cyanuric iodide is not known to be similarly constituted.

**Cyanuric Chloride.**  $(\text{CNCl})_3$  is formed by the polymerisation of cyanogen chloride, which takes place spontaneously in presence of a little hydrochloric acid.<sup>3</sup> This polymerisation may be accounted for by the chloramino-structure of cyanogen chloride,  $\text{C} \begin{smallmatrix} \text{N} \\ \diagup \end{smallmatrix} \text{Cl}$ , whose molecules combine with hydrogen chloride to form the hydrochloride  $\text{H} \begin{smallmatrix} \text{N} \\ \diagup \end{smallmatrix} \text{C} \begin{smallmatrix} \text{N} \\ \diagup \end{smallmatrix} \text{Cl}$ , three molecules of which condense, with elimination of  $3\text{HCl}$  thus<sup>4</sup>—



The polymer is also formed when chlorine acts on hydrocyanic acid in presence of sunlight<sup>5</sup> or upon a chloroform solution of the same substance containing 1 per cent. of alcohol<sup>6</sup>; it also results from the action of phosphorus pentachloride on cyanuric acid,<sup>7</sup>  $(\text{CNOH})_3$ .

Cyanuric chloride consists of colourless, monoclinic crystals which melt at  $145^\circ\text{C}$ , forming a liquid boiling at  $190^\circ\text{C}$ ,<sup>5</sup> the vapour density<sup>8</sup>

<sup>1</sup> See Kovalik *Zeits. physikal. Chem.*, 1912, 80, 107.

<sup>2</sup> Kastle and Clark, *Ann. Chem. Phys.*, 30, 87.

<sup>3</sup> Huntzschel *Mon. Ber.*, 1895, 28, 414.

<sup>4</sup> Clutton-Bow and Woburn, *Trans. Chem. Soc.*, 1902, 81, 194.

<sup>5</sup> Gauthier, *Ann. Chem. Phys.*, 1867, 74, 122.

<sup>6</sup> Diels *Ber.*, 1891, 32, 692.

<sup>7</sup> Bailem, *Ann. Chem. Phys.*, 1890, 116, 357.

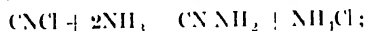
<sup>8</sup> Bureau, *Ann. Chem. Phys.*, 1838, 68, 124, 1839, 70, 261.

is 6.35, which corresponds to the formula  $(\text{CNCl})_3$ . The heat of formation of  $(\text{CNCl})_4$  from its elements is 107,900 calories; its heat of polymerisation from liquid  $\text{CNCl}$  is 28,700 calories; its heat of combustion 292,000 calories.<sup>1</sup> Cyanine chloride dissolves in alcohol, chloroform, and other organic solvents without decomposition; water or moist air hydrolyses it into cyanine and hydrochloric acids.

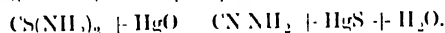
**Cyanine Bromide**,  $(\text{CNBr})_3$ , resembles cyanine chloride. It is formed from impure cyanogen bromide at 130–140° C.,<sup>2</sup> and in 70–80 per cent. yield by the action of nascent hydrogen bromide on a benzene solution of cyanogen bromide;<sup>3</sup> it is also obtained by the action of bromine on potassium ferri-cyanide.<sup>4</sup> It is a white, amorphous powder which melts at 300° C., and is hydrolysed by water into cyanine and hydrobromic acids.

**Cyanine Iodide**,  $(\text{CNI})_3$ , is formed as a dark-brown amorphous powder by the action of hydroiodic acid on cyanine chloride. It is decomposed above 200° C. into iodine and paracyanogen; consequently its molecular constitution is unknown. Hot water hydrolyses it into cyanine and hydroiodic acids.

**Cyanamide**,  $\text{CN NH}_2$ . Cyanamide is formed according to a common way of preparing amides, by the action of ammonia on the chloride<sup>5</sup>,

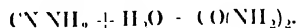


it is also conveniently obtained from thiourea by the removal from it of  $\text{H}_2\text{S}$  through the agency of precipitated mercuric oxide:



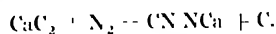
The mercuric oxide is added to an aqueous solution of thiourea until a drop of the liquid ceases to darken ammoniacal silver nitrate solution by formation of  $\text{Ag}_2\text{S}$ . The filtered solution is then evaporated and extracted with ether, whence cyanamide crystallises.

Cyanamide melts at 40° C., and can be distilled at 113–114° C. under 18 mm. pressure. It is deliquescent, is volatile in steam, and is converted by very dilute nitric acid into urea.



Like the amides of other weak acids, cyanamide possesses both basic and acidic properties. The dihydrochloride,  $\text{CN NH}_2 \cdot 2\text{HCl}$ , is formed as a crystalline powder when hydrogen chloride gas is passed into an ethereal solution of cyanamide; on the other hand, the di-silver salt  $\text{CN NAg}_2$  is precipitated as a yellow powder when ammoniacal silver nitrate is added to an aqueous solution of cyanamide. Likewise the monosodium salt  $\text{CN NHNa}$  is formed when sodium ethoxide reacts with alcoholic cyanamide.

**Calcium cyanamide** mixed with carbon is produced, rather than calcium cyanide, when nitrogen is passed over calcium carbide heated in an electric furnace:



<sup>1</sup> Lemoult, *Ann. Chim. Phys.*, 1899, [vi], 16, 338.

<sup>2</sup> Ephus, *Ber.*, 1869, 2, 159; Panaretow, *Ber.*, 1885, 18, 1261.

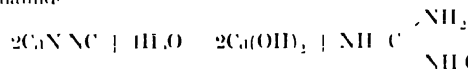
<sup>3</sup> Meyer and Nabe, *J. prakt. Chem.*, 1910, [ii], 82, 521.

<sup>4</sup> Metz and Werth, *Ber.*, 1883, 16, 2894.

<sup>5</sup> Bineau, *Ann. Chim. Phys.*, 1838, [ii], 67, 368–1839, [ii], 70, 251. Cloez and Cannizzaro, *Compt. rend.*, 1851, 32, 62.

<sup>1</sup>The product known as "Kalkstickstoff" or "Nitrohm" is employed as a nitrogenous manure.<sup>1</sup>

Calcium cyanamide is hydrolysed by cold water with the formation of dicyanamide:



When carbon dioxide is passed through this solution calcium cyanamidocarbonylate,  $\text{CaN}_2\text{C}(\text{CO})\text{O} \cdot 2\text{H}_2\text{O}$ , is produced.

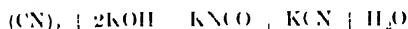
Under the influence of heat cyanamide polymerises<sup>2</sup> to dicyanamide,  $\text{NH}_2\text{C}(\text{NH}_2)_2$ , and cyanonitrile,  $(\text{CN} \cdot \text{NH}_2)_2$ .

#### CYANIC ACID AND RELATED COMPOUNDS

There are four compounds having the empirical formula  $\text{HCNO}$ :

$\text{OC}(\text{NH})$	iso-cyanic acid
$\text{C}(\text{N})\text{OH}$	fulminic acid
$(\text{CONH})_2$	cyanuric acid
$(\text{CONH})_4$	cyanuric diide

**Cyanic Acid.** Potassium cyanate is formed, together with cyanide, when cyanogen reacts with potash:



The same salt is produced by the oxidation of fused cyanide by the air or a reducible oxide such as red lead, also by heating potassium dichromate with anhydrous potassium ferrocyanide, and extracting the melt with ethyl alcohol containing a little methyl alcohol.<sup>3</sup> Sodium cyanate is formed, together with other products, when sodium nitrate is heated with carbon.<sup>4</sup> Cyanic acid cannot be isolated by liberation from potassium cyanate, because it is unstable in aqueous solution, taking up the elements of water to form ammonium hydrogencarbonate:  $\text{CONH} + 2\text{H}_2\text{O} = \text{NH}_4\text{HCO}_3$ . Consequently a cyanate effervesces with dilute hydrochloric acid like a carbonate.

Cyanic acid may, however, be obtained by heating cyanuric acid in a current of carbon dioxide and condensing the evolved vapour in a freezing mixture. Thus obtained, at low temperature, cyanic acid is found to be a colourless, volatile liquid, which has a density of 1.1538 at  $-20^\circ\text{C}$ . and 1.110 at  $0^\circ\text{C}$ . It has a pungent smell resembling that of acetic acid. Its vapour density at  $110^\circ\text{C}$ . is 1.50 (air = 1), which supports the monomolecular formula,  $\text{CONH}$ . The heat of formation of cyanic acid from its elements (C as diamond) is about 37,000 calories.<sup>5</sup> At atmospheric temperature cyanic acid passes, with evolution of heat, into the solid polymer cyanuric diide, whence cyanic acid is recovered by

<sup>1</sup> Cuno, *Z. Anorg. Chem.*, 1910, 23, 2105.

<sup>2</sup> Chown, *Gazette*, 1908, 38, ii, 358.

<sup>3</sup> Haug, *Annalen*, 1862, 122, 22.

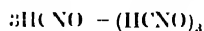
<sup>4</sup> Bell, *Chem. News*, 1875, 32, 19; Erdmann, *Ber.*, 1893, 26, 2438.

<sup>5</sup> Ladoff, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 651.

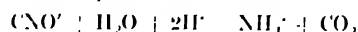
<sup>6</sup> Berthelot, *Compt. rend.*, 1896, 123, 337.

vaporisation. Aqueous cyanic acid is subject to three types of change<sup>1</sup>:

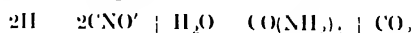
I. Polymerisation of the non-ionised acid in concentrated solution



II. Decomposition in presence of an acid.



III. Spontaneous decomposition of dilute solution.

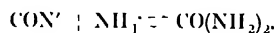


*Constitution of Cyanic Acid*—Since the isomeric fulminic acid is  $\text{C} \equiv \text{N} \cdot \text{OH}$ , there remain two possible formulae for cyanic acid:  $\text{N} \equiv \text{C} \cdot \text{OH}$  and  $\text{O} = \text{C} \equiv \text{NH}$ , the former of which might be called normal and the latter iso-cyanic acid. The normal acid appears, however, not to exist either in the free state or in the form of its salts or esters.<sup>2</sup> Cyanic acid and the cyanate, therefore, are iso-compounds, and are indeed carbonamide and its derivatives. Nevertheless the name cyanic, rather than isocyanic, acid is usually employed for this acid. Michael and Hibbert<sup>3</sup> support the conclusion that the cyanic acid both in the state of vapour and in solution is carbonamide,  $\text{CO} \cdot \text{NH}$ .

The relation of cyanic acid,  $\text{CONH}$ , to its two polymers, cyanuric acid,  $(\text{CONH})_3$ , and cyanuride,  $(\text{CONH})_6$ , is an interesting one, and forms a valuable subject for study from the standpoint of the phase rule. The relationship between the vapour of cyanic acid and its two solid forms has been investigated by van't Hoff,<sup>4</sup> who has found that the triple point at which these three phases are in equilibrium is at  $150^\circ \text{C}$  under 50 mm. pressure. As previously stated, it is only when cyanic acid vapour is rapidly cooled in a freezing mixture that the unstable liquid cyanic acid is produced.

Cyanic acid forms an additive compound with hydrochloric acid, and is reduced by nascent hydrogen to formamide,  $\text{HCONH}_2$ .

*The Cyanates*—Ammonium cyanate is an interesting salt, because Wohler in 1828 observed its transformation into urea, and thus showed that an "organic" compound could be obtained from an inorganic source without the intervention of "vital force." If a solution of potassium cyanate, a salt obtained by the oxidation of potassium cyanide by fusion with red lead, is evaporated to dryness with an equivalent quantity of ammonium sulphate, urea is formed from the resulting ammonium cyanate, and may be extracted with alcohol from the residue, leaving potassium sulphate. The reaction, which is bi-molecular, since it takes place between cyanate and ammonium ions, may be represented thus



The dynamics of this reaction has been studied by Walker.<sup>5</sup> Walker

<sup>1</sup> Normand and Cumming, *Trans. Chem. Soc.*, 1912, **101**, 1852.

<sup>2</sup> Nef, *Annalen*, 1893, **287**, 296.

<sup>3</sup> Michael and Hibbert, *Annalen*, 1909, **361**, 129.

<sup>4</sup> Van't Hoff, *Studies in Chemical Dynamics*, Eng. edn., 1896 (Williams and Norgate), pp. 37 et seq.

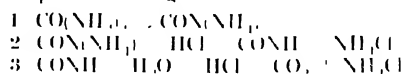
<sup>5</sup> Walker, *Trans. Chem. Soc.*, 1895, **67**, 716, *Zetsch physikal. Chem.*, 1902, **42**, 207.

and Appleby,<sup>1</sup> Fawcitt,<sup>2</sup> and Walker and Kay.<sup>3</sup> The transformation of ammonium cyanate, in the state of its ions, into urea is accompanied by a heat evolution of 5000 calories per gram molecule.

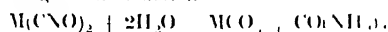
By the action of hydrochloric acid urea undergoes the following reaction:



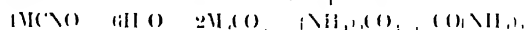
which is made up of these stages:



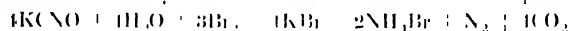
Metallic cyanates are hydrolysed by hot water into carbonates and urea according to the reaction:



The reaction takes place in two stages: (i) a slow hydrolysis of CNO' ions yielding carbonate and NH<sub>4</sub><sup>+</sup> ions, (ii) interaction of NH<sub>4</sub><sup>+</sup> and CNO' to form urea. The cyanates of sodium and potassium are hydrolysed by water according to the equation<sup>4</sup>:

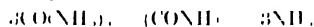


Bromine reacts with potassium cyanide according to the equation:



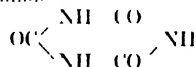
Silver, lead, mercury, and cupric cyanates are white precipitates, practically insoluble in water.

**Cyanuric Acid**, (CONH)<sub>3</sub>, is produced by the condensation of cyanic acid (above 159° C.) by the action of ammonia on phosgene (COCl<sub>2</sub>), and by heating urea above its melting-point as long as ammonia is evolved (Wohler). The reaction:



depends upon the formation of ammonium cyanate, followed by the loss of ammonia and polymerisation of three molecules of cyanic acid thus set free. The use of anhydrous zinc chloride promotes the formation of cyanuric acid.<sup>5</sup> Cyanuric acid is also produced by chlorinating<sup>6</sup> or brominating<sup>7</sup> urea, and hydrolysing the resulting cyanuric halide. The acid crystallises from concentrated sulphuric acid in anhydrous quadratoctahedra and from water in dihydrated monoclinic prisms.

The formation of this acid from urea suggests that it possesses an imide rather than a hydroxybe constitution, and this view is borne out by the character of its absorption spectrum.<sup>8</sup> Cyanuric acid is therefore, probably, triacetonimide:



<sup>1</sup> Walker and Appleby, *Trans. Chem. Soc.*, 1896, 65, 191.

<sup>2</sup> Fawcitt, *Proc. Chem. Soc.*, 1900, 85, 1881; 1901, 87, 191; *Z. physikal. Chem.* 1902, 11, 601.

<sup>3</sup> Walker and Kay, *Trans. Chem. Soc.*, 1901, 11, 207.

<sup>4</sup> O and F. Mason, *Z. physikal. Chem.*, 1911, 70, 590.

<sup>5</sup> Norrish and Chinnery, *Trans. Chem. Soc.*, 1912, 161, 1852.

<sup>6</sup> Wohler, *Monatsh. Chem.*, 1909, [1909], 126.

<sup>7</sup> Smolka, *Monatsh.*, 1887, 3, 65.

<sup>8</sup> Wurtz, *Compt. Rend.*, 1847, 61, 307.

<sup>9</sup> Hantz, *Proc. Chem. Soc.*, 1899, 15, 16; 1900, 16, 129.



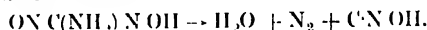
Anhydrous cyanuric acid has a density of 1.768 at 0° C.; it does not melt, but sublimes above 150° C., producing cyanic acid vapour; at 350° C. it decomposes.

The heat of formation<sup>1</sup> of cyanuric acid from liquid cyanic acid is 37,000 calories, and from its elements 166,100 calories; its heat of combustion is 220,000 calories. One hundred parts of water dissolve 0.125 parts of cyanuric acid at atmospheric temperature, and 4 parts at 100° C.; the acid is readily soluble in alcohol.

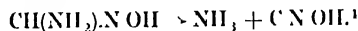
Cyanuric acid is a very weak tribasic acid whose aqueous solution does not affect indicators; its tri- and di-alkali salts are much hydrolysed by water, and are converted by carbon dioxide into the mono-salt.

**Cyameliide**, (CONH)<sub>3</sub>, a polymer of cyanic acid of unknown molecular weight, is formed from this acid at 0° C. by spontaneous polymerisation with evolution of heat and light, and may also be prepared by gently heating a mixture of equal parts of potassium cyanate and oxalic acid. It is a white amorphous powder, which, in accordance with high molecular weight, is insoluble in water and other solvents; its density at 0° C. is 1.974<sup>2</sup>; its heat of formation per gram is 1362 calories; and its heat of combustion 1630 calories. The heat of transformation of cyameliide into cyanuric acid is - 9600 calories. Cyameliide dissolves in alkalis, forming cyanates; it dissolves in sulphuric acid unchanged, whence it may be precipitated by water, but when warmed with the concentrated acid it passes into cyanuric acid, and eventually into carbon dioxide and ammonia.

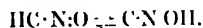
**Fulminic Acid**, CNOH, formed the subject of the first investigation of isomerism by Liebig and Wohler, since its salts were found to possess an identical qualitative and quantitative composition with those of cyanic acid. The mercuric salt of this acid is prepared by adding alcohol to a solution of mercury in excess of nitric acid, and the acid itself, which is exceedingly unstable, is obtained in ethereal solution when its mercuric salt, suspended in ether, is decomposed with dry hydrogen chloride. Fulminic acid is also formed and its silver salt obtained when ammoniumthylinitrosolic acid decomposes in presence of nitric acid and silver nitrate:



Methylenamino-oxime, when treated with nitric acid and silver nitrate, also yields silver fulminate.



It has been shown by Neef<sup>5</sup> and Scholl<sup>6</sup> that the acid is carbonyloxime, C=N-OH; Palazzo,<sup>7</sup> however, regards it as tautomeric and a pseudo-acid.



It is named fulminic acid on account of its explosive properties, and its mercuric salt is much employed for the manufacture of detonators

<sup>1</sup> Lemoine, *Compt. rend.*, 1871, 121, 351.

<sup>2</sup> Scholl, *Annalen*, 1896, 291, 376.

<sup>3</sup> Troost and Hauteville, *Compt. rend.*, 1869, 69, 49.

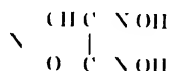
<sup>4</sup> Wieland, *Ber.*, 1909, 42, 820.

<sup>5</sup> Neef, *Annalen*, 1891, 280, 503.

<sup>6</sup> Scholl, *Ber.*, 1900, 33, 51; 1901, 34, 1441; 1903, 36, 10.

<sup>7</sup> Palazzo, *Atti R. Accad. Lincei*, 1912 [v], 21 n. 713.

and explosive caps. In accordance with its explosive character, this acid is endothermic, the mercuric salt liberating 116,000 calories per gram molecule on its decomposition into mercury, nitrogen and carbon monoxide. By the action of concentrated hydrochloric acid on mercuric fulminate the oxime of chloroformaldehyde,  $\text{H}_2\text{C}(\text{Cl})\text{NOH}$ , results, whilst dilute acid produces hydroxylamine and formic acid. The spontaneous polymerisation of fulminic acid yields methylfulminic acid (isocyanic acid), which is probably <sup>1</sup>

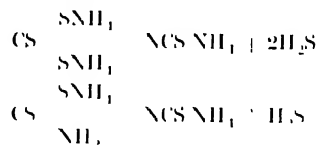


**Thiocyanic Acid** (*Sulphocyanic Acid*)  $\text{HSCN}$ . The potassium salt of this acid was first prepared in 1808 by Berzelius by boiling potassium sulphide solution with prussic blue; it was examined quantitatively by Berzelius in 1820.<sup>2</sup>

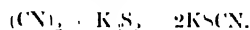
The salts of the acid are formed by the direct union of cyanides with sulphur, either by fusion or by evaporating their aqueous solutions with polysulphide. They may also be prepared from complex cyanides; potassium thiocyanate, for instance, is obtained by heating together potassium ferrocyanide, potassium carbonate and sulphur. Ammonium thiocyanate is formed by warming together hydrocyanic acid and yellow ammonium sulphide solutions.



and is thus prepared from the cyanide formed in gas manufacture. It may also be obtained by the interaction of carbon disulphide and an alcoholic solution of ammonia. When 350-400 grams of carbon disulphide are mixed with 600 grams of 95 per cent. alcohol and 800 grams of ammonia solution of 0.942 density, there is formed on standing a mixture of ammonium thiocarbonate and thiocarbamate; and these on heating yield thiocyanate, thus



Potassium thiocyanate may also be prepared by passing cyanogen gas over heated potassium disulphide



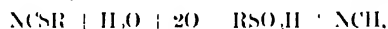
Thiocyanic acid may be obtained in solution by decomposing barium thiocyanate with an equivalent quantity of dilute sulphuric acid, or in the anhydrous state by distilling its potassium salt with dilute sulphuric or phosphoric acid, passing the vapour through a long calcium chloride tube, and then condensing it in a freezing mixture. A better way is to drop concentrated sulphuric acid on to a mixture of potassium thiocyanate and phosphoric oxide in an atmosphere of

<sup>1</sup> Wieland and Hess, *Ber.*, 1909, 42, 1346.

<sup>2</sup> Berzelius, *Schwedger's J.*, 1820, 31, 42.

hydrogen<sup>1</sup>. The acid distils over under a pressure of 40-60 mm. The acid may also be obtained from its insoluble salts, such as those of lead and mercury, by decomposing them with hydrogen sulphide. At ordinary temperature thiocyanic acid, whose vapour is stable, is a clear, yellowish, volatile, oily liquid of unknown boiling-point, which when sufficiently cooled forms colourless crystals, stable in dry hydrogen at  $-15^{\circ}\text{C}$ , which melt at  $-5^{\circ}\text{C}$  and readily decompose, with evolution of heat, into hydrocyanic acid and isothiocyanic acid,  $\text{C}_2\text{N}_2\text{S}_2\text{H}_2$  (*qv*). The acid is soluble in ether, and is stable in dilute aqueous solution. Cryoscopic measurements in benzene, etc., indicate a mixture of single and double molecules.

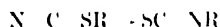
Thiocyanic acid may be represented by the formula  $\text{N} \equiv \text{C} \cdot \text{SH}$  or  $\text{SC} \cdot \text{NH}$ . Probably the mercuric salts have the constitution represented by the first formula, as well as the esters derived from them. These esters are converted into sulphonic acids and hydrocyanic acid by oxidation:



and are reduced by nascent hydrogen to mercaptans:



They can, however, undergo isomeric change into the esters of isothiocyanic acid, which are the mustard oils:



This change is accompanied by the evolution of heat, which for the methyl ester amounts to  $-6800$  calories.<sup>2</sup>

Measurements of the molecular refraction of thiocyanates have been made by Dixon and Taylor.<sup>3</sup>

The heat of formation of thiocyanic acid in aqueous solution from its elements is  $-19,900$  calories, and from  $\text{HCNaq}$  is  $+5800$  calories.<sup>4</sup>

An aqueous solution of thiocyanic acid is largely ionised and approaches hydrochloric acid in strength.

Below are given the conductivity ( $\gamma$ ) and degree of dissociation ( $\gamma$ ) at various dilutions (c litres) and  $25^{\circ}\text{C}$ , whence the constant  $K$  is calculated.<sup>5</sup>

$c$	$\lambda_c$	$\gamma$	$K$
2	326	0.88316	1.71
4	337	0.91328	1.81
8	345	0.93495	1.75
16	352	0.95392	1.91
512	369	1.00000	
			Mean 1.81

<sup>1</sup> Rosenheim and Levy, *Ber.*, 1907, 40, 2166; see also Rack and Stenmetz, *Zeitsch. anorg. Chem.*, 1912, 77, 51.

<sup>2</sup> Thomsen, *Thermochemische Untersuchungen*, 1886, vol. iv.

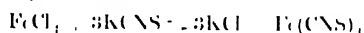
<sup>3</sup> Dixon and Taylor, *Trans. Chem. Soc.*, 1910, 97, 927.

<sup>4</sup> Joannes, *Compt. rend.*, 1882, 94, 797.

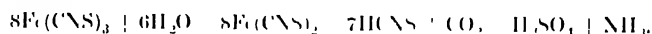
<sup>5</sup> Ostwald, *Lehrbuch der allgem. Chem.*, 1903, ii, 1, 729; Rudolph, *Zeitsch. physikal. Chem.*, 1895, 17, 393.

*Silver Thiocyanate* is a curdy white precipitate resembling silver chloride, and insoluble in nitric acid; *cuprous thiocyanate*, formed by adding thiocyanate solution to copper sulphide in presence of sulphurous acid, is also a white precipitate.

*Ferrie Thiocyanate* is the blood-red substance formed in solution in the well-known test for iron. This reaction has been the subject of extended investigation by Bongiovanni<sup>1</sup> who has shown that it may be quite simply represented thus:



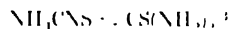
the colour being due to non-ionised  $\text{Fe}(\text{CNS})_2$  and its intensity depending on the product of the concentrations of ferrie and thiocyanate ions. The decolouration on dilution is due to hydrolysis of non-ionised  $\text{Fe}(\text{CNS})_2$  into yellow, colloidal ferrie hydroxide and thiocyanic acid. Philip and Bramley<sup>2</sup> however confirm the judgment of other observers that loss of colour is associated with reduction of iron, and show that the following equation approximately represents the change in aqueous solution:



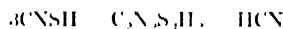
The discharging of the colour by oxalate, tetrates, etc., is caused by the formation of complex ions with the ferrie ions of the ionised ferrie thiocyanate, which causes further ionisation of the red non-ionised salt and consequent loss of colour.

Molybdenum and vanadium thiocyanates are also red and behave similarly to the ferrie salt.

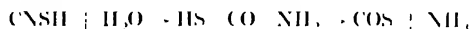
*Mercuric Thiocyanate*, formed as a white precipitate when mercuric chloride and potassium thiocyanate solutions are mixed together, is soluble in excess of either solution. When dried this salt is inflammable, and in burning forms a voluminous residue known as "Pharaoh's serpents". *Ammonium thiocyanate* is converted when heated in the fused state into thiourea:



When moderately concentrated sulphuric or hydrochloric acid is warmed with alkali thiocyanate a yellow solid separates, and carbonyl sulphide gas is evolved which burns with a pale sulphurous flame. The yellow substance contains isopropylthiocyanic acid, formed, together with hydrocyanic acid, according to the reaction:



The carbonyl sulphide is produced together with ammonia, by the hydrolysis of thiocyanic acid which, according to Klason<sup>3</sup> is preceded by the formation of thiolethanne acid, thus:



Besides these products there are others, including hydrogen sulphide

<sup>1</sup> Bongiovanni, *Gazzetta* 1907, 37, 1, 172; 1908, 38, 5, 209; *Bull. chem. farm.*, 1910, 49, 789.

<sup>2</sup> Philip and Bramley, *Trans. Chem. Soc.*, 1913, 103, 797.

<sup>3</sup> Beaudou and Werner, *Trans. Chem. Soc.*, 1903, 83, 1; Soudy and Kettner, *Proc. K. Akad. Wissensch. Vindobona*, 1912, 18, 683.

<sup>4</sup> Klason, *J. prakt. Chem.*, 1887, [a], 36, 77; 1888, 38, 383.

and sulphur, which react with thioevanic acid to produce the disulphide

of thialthioncarbanic acid  $\left( \text{SC} \begin{array}{c} \nearrow \text{SH} \\ \searrow \text{NH}_2 \end{array} \right)$ , thus :



This compound, however, decomposes on warming, yielding ammonium thiocyanate, carbon disulphide, and sulphur, thus :

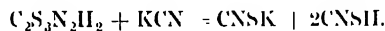


By the action of zinc and hydrochloric acid thioevanic acid is reduced to trithioformaldehyde, ammonia, methylamine, hydrogen sulphide, and hydroevanic acid.<sup>1</sup>

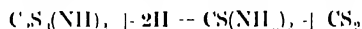
Bromine oxidises thioevanate quantitatively in aqueous solution, thus<sup>2</sup> :



**Isoperthiocyanic Acid**,  $\text{C}_2\text{S}_3(\text{NH})_2$ , as stated above, is formed by the action of acid of moderate strength *e.g.* 40 per cent. hydrochloric acid on ammonium thiocyanate. It can be crystallised from water in golden-yellow needles, and is reconverted by potassium cyanide into thiocyanate :



That it is probably an iso-acid containing imide groups is shown by its reduction by nascent hydrogen to thionca and carbon disulphide :



Salts of the isomeric normal perthioevanic acid,  $\text{C}_2\text{N}_2\text{S}(\text{SH})_2$ ,<sup>3</sup> are formed by the action of alkalis on the iso-acid, but the free acid

is unstable. Normal and iso-dithioevanic acid  $\text{HS} \begin{array}{c} \nearrow \text{N} \\ \searrow \text{N} \end{array} \text{CSH}$  and  $\text{SC} \begin{array}{c} \nearrow \text{NH} \\ \searrow \text{NH} \end{array} \text{CS}$  respectively, are also known ; as well as trithioevanic

acid,  $(\text{CNSH})_3$ , which is formed by the interaction of cyanuric chloride and alkali sulphide.<sup>4</sup>

**Detection and Estimation of Thiocyanate.** - A thiocyanate is detected by its behaviour with acid described above, and by the blood-red colour produced with ferric chloride, which is discharged by mercuric chloride, owing to the formation of the complex salt  $\cdot \text{HgCNS} \cdot \text{HgCl}_2$ .

It may be estimated gravimetrically by precipitation as cuprous thiocyanate, or by oxidation by permanganate to sulphate, which is precipitated with barium chloride.<sup>5</sup> Volumetrically, thiocyanate is estimated by Volhard's method, in which its solution is titrated into standard silver nitrate solution, containing nitric acid and a little ferric sulphate to indicate by means of a red colour when the thiocyanate has been added in excess.

It is also said to be possible to titrate cuprous thiocyanate with

<sup>1</sup> Hofmann, *Ber.*, 1867, **1**, 179.

<sup>2</sup> Koenig, *J. prakt. Chem.*, 1911, [n], **84**, 558.

<sup>3</sup> Klatson, *J. prakt. Chem.*, 1887, [n], **36**, 57 ; 1888, **38**, 383.

<sup>4</sup> Hofmann, *Ber.*, 1880, **13**, 1851 ; 1885, **18**, 2201.

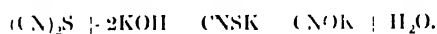
<sup>5</sup> Alt, *Ber.*, 1889, **22**, 3258, but see Grossmann and Holter, *Chem. Zeit.*, 1909, **33**, 348.

permanganate after dissolving it in ammonia, and acidifying the solution with dilute sulphuric acid.<sup>1</sup>

**Cyanogen Sulphide** (*Thiocyanic Anhydride*),  $(\text{CN})_2\text{S}$ —This compound results from the interaction of silver thiocyanate and cyanogen iodide. It is formed in ethereal solution consequent on the separation of the very insoluble silver iodide.<sup>2</sup>



The sulphide crystallises from carbon disulphide solution at  $0^\circ \text{C}$  in rhombic tablets which sublime above  $30^\circ \text{C}$ , and melt at  $60^\circ \text{C}$ , and dissolve in water, alcohol and ether, but are decomposed by alkalis, like other thiocyanhydrides, into a mixture of thio- and oxy-salts.



Cyanogen selenide,  $(\text{CN})_2\text{Se}$ , also exists.<sup>3</sup>

<sup>1</sup> Roulet *Ann. Chim. Phys.* 1911, 16, 336.

<sup>2</sup> Laurent *Annalen*, 1819, 70, 36.

<sup>3</sup> Schneider *Proc. Acad.* 1866, 129, 304.

## CHAPTER III

### SILICON AND ITS COMPOUNDS

#### SILICON

Symbol, Si. Atomic weight, 28.3 (O = 16)

**Occurrence of Silicon.** Although not occurring naturally in the free state upon the earth, silicon is, next to oxygen, the most plentiful of the elements. It is always found combined with oxygen as silica, which exists in various forms either in the free state, or united with water or with metallic oxides, forming the numerous and frequently complex silicates of which the primitive rocks of the earth's crust so largely consist. Through the medium of water, silica is assimilated by certain plants<sup>1</sup> and animal organisms<sup>2</sup>; its presence has been detected in the sun and many stars, as well as in meteorites, as, for instance, that of the Diablo Cañon.

**History.** The history of silicon and its compounds commences with the observation of Becher that siliceous minerals are suitable for glass-making, and contain an "earth" which he named *terra chalcabitis*. In 1660 Tachemius found that this "earth" combines with alkalis, and therefore possesses an acid nature. Further knowledge of the element was gained by Scheele, who in 1771 prepared hydrofluoric acid, and thence silicon tetrafluoride, which with water yielded silicic and hydrofluosilicic acids. The decomposition of the alkalis and alkaline earths in 1808 by Davy led to the belief that silica is also a compound; and in the same year Berzelius obtained what he believed to be silicon ("kiesel") by heating iron, carbon, and silica together.

Gay Lussac and Thénard<sup>3</sup> were probably the first, however, to obtain the element. This they did in 1811, by passing silicon tetrafluoride over heated potassium; whilst Berzelius,<sup>4</sup> in 1823, decomposed potassium silicofluoride<sup>5</sup> with potassium, and obtained what Vigouroux<sup>6</sup> has shown to be impure silicon. Our knowledge of amorphous and crystallised silicon is due principally to the researches of Wohler and St. Claire-Deville,<sup>7</sup> Moissan and Smiles,<sup>8</sup> and Vigouroux.<sup>9</sup>

<sup>1</sup> Berthelot and Audier, *Ann. Chim. Phys.*, 1892, [vi], 27, 145.

<sup>2</sup> Schultz, *Munch. Med. Wochenschr.*, 1902, 110; *Pflüger's Archiv*, 1901, 84, 67; 1902, 89, 112.

<sup>3</sup> Gay Lussac and Thénard, see *Recherches physico-chimiques*, 1811, i, 313, n. 53.

<sup>4</sup> Berzelius, *Pogg. Annalen*, 1823, i, 169.

<sup>5</sup> The Author prefers this nomenclature to the more usual term *silicofluoride*. The salt is not a silicous derivative. Although silicous derivatives are not known to exist, that is no justification for borrowing their nomenclature. Even if "silicofluoride" is a corruption of "silicon fluoride," which is probable, it is better to adopt a nomenclature which is consistent throughout. Compare, for example, with  $K_2SiF_6$  the stannofluoride,  $K_2SnCl_6$ , also the platino- and platinum-chlorides,  $K_2PtCl_6$  and  $K_2PtCl_4$ , respectively, etc.

<sup>6</sup> Vigouroux, *Ann. Chim. Phys.*, 1897, [vi], 12, 5.

<sup>7</sup> Deville, *Ann. Chim. Phys.*, 1856, [iii], 49, 66.

<sup>8</sup> Moissan and Smiles, *Compt. rend.*, 1893, 116, 1129; 1902, 134, 1552; 1901, 138, 1299.

<sup>9</sup> Vigouroux, *Compt. rend.*, 1896, 123, 115; *Ann. Chim. Phys.*, 1897, [vi], 12, 153.

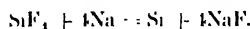
**Chemical Characteristics and Relationships.**—Silicon forms with boron and carbon a little group of non-metals, which in the elementary state are characterised by distinct allotropy accompanied by high molecular complexity, so that not only are the elements non-volatile, even at high temperature, but they are, for the same reason, comparatively inert towards chemical reagents. Silicon in combination, like carbon, is almost invariably quadrivalent; though it appears that silica is reducible to a lower state of oxidation in which the element is bivalent. Silicon is one of the least electronegative of the non-metals, and forms compounds with other non-metals more readily than with metals; moreover, silicic acid is a very weak acid, and shares with boric, stannic, and some other acids the tendency to form condensed acids.

Silicon is the second member of the fourth group of the Periodic system; thus it occupies a position in the centre of the second short period. Like its neighbours in this period, it shows a relationship to the first member of the group—in this case carbon—which is by no means close, since all the members of the first short period show unique characteristics, which separate them from the rest of the elements. Especially is this the case with carbon, to which silicon, even with our extending knowledge of its capabilities, will probably never be found to bear any close relationship. The relationship between silicon and other elements has been fully discussed in the introductory chapter.

**Preparation and Properties of Silicon.** Silicon exists in two distinct allotropic forms: amorphous and crystalline. Several varieties both of amorphous and crystalline silicon have been described, but it is doubtful whether they should be regarded as distinct allotropic forms.

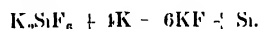
**Amorphous Silicon.** *Preparation.* Amorphous silicon may be prepared in various ways, nearly all of which consist in reducing silicon compounds with metals.

(1) Silicon fluoride or chloride may be reduced by sodium or potassium, e.g.:



Gay Lussac and Thénard<sup>1</sup> passed silicon tetrafluoride gas over heated potassium, and Deville<sup>2</sup> employed silicon tetrachloride vapour and sodium, whilst Hempel and von Haas<sup>3</sup> passed silicon tetrafluoride on to sodium heated to 100°–500° C. in a cast-iron crucible, and allowed the mass to cool in a current of silicon tetrafluoride, so that sodium silicofluoride,  $\text{Na}_2\text{SiF}_6$ , was formed, which was easily separated from the silicon by means of water.

(2) A slight modification consists in reducing a silicofluoride with sodium or potassium, thus:



This reaction was employed by Berzelius<sup>4</sup> in 1823, who heated the reagents together in an iron tube, and subsequently removed the

<sup>1</sup> Gay Lussac and Thénard, *Recherches physico-chimiques*, 1811, i, 313, ii, 53.

<sup>2</sup> Deville, *Ann. Chim. Phys.*, 1857, [iii], 49, 68.

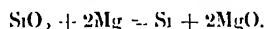
<sup>3</sup> Hempel and von Haas, *Zeitsch. angew. Chem.*, 1900, 23, 32.

<sup>4</sup> Berzelius, *Pogg. Annalen*, 1824, i, 169.

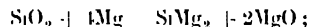


potassium fluoride by water. Wohler<sup>1</sup> employed sodium silicifluoride and sodium, and heated the mixture, covered with common salt, in a clay crucible.

(3) A further method consists in reducing silica by heating it with a metal. Potassium and sodium were employed, but without great success; powdered magnesium has, however, been found to be a suitable reducing agent, and the reaction may be carried out as follows<sup>2</sup>: Powdered quartz or thoroughly dried<sup>3</sup> precipitated silica is mixed with magnesium powder in the proportions required for the reaction:



and a quarter of the weight of calcined magnesia is added.<sup>4</sup> The mixture is heated in a clay crucible, first at 300°–400° C., further to ensure thorough drying, and then at a red heat. The reaction quickly occurs with evolution of much heat; and, after cooling, the silicon is isolated by treating the mass with hydrochloric acid to dissolve the magnesia, and with hydrofluoric and sulphuric acids to remove the remaining silica; the silicon is then washed with water and dried in a current of hydrogen. If the reaction became too violent there would be a tendency for the reduced silicon to combine with the unchanged magnesium to form silicide according to the reaction



thus the silicon formed would be diminished in quantity, and would be impure. The magnesia is added to retard the reaction; and by its means the silicon obtained is of 96.97 per cent. purity.

As a laboratory experiment silicon may be prepared by heating in a hard glass tube 4 parts by weight of thoroughly dried powdered white sand with 1 part of magnesium powder.<sup>5</sup>

(4) Amorphous silicon is produced when electric sparks are passed through liquid silico-ethane,<sup>6</sup>  $\text{Si}_2\text{H}_6$ ; and thus obtained, possesses the power of reducing cold neutral potassium permanganate solution and boiling copper, gold, and mercuric solutions.

*Properties of Amorphous Silicon.*—Pure, amorphous silicon, prepared from silica by means of magnesium, according to the method of Vigouroux, is a brown, hygroscopic powder with a density of 2.35 at 15° C. and a specific heat<sup>7</sup> of 0.214 at 21° C., which is greater than that of crystallised silicon. Cambi has obtained another variety of amorphous silicon of a reddish-yellow colour and density 2.08, and considers that the different amorphous silicones are not clearly defined allotropic forms, but masses of forms possibly possessing different molecular structures.<sup>8</sup> According to Wilke-Dorfurt,<sup>9</sup> a less reactive, grey form

<sup>1</sup> Wohler, *Annalen*, 1857, 104, 167.

<sup>2</sup> Vigouroux, *Ann. Chim. Phys.*, 1897, [vii], 12, 5.

<sup>3</sup> Unless the silica is thoroughly dried a dangerous explosion may occur, especially if precipitated silica is employed. See Gattermann, *Ber.*, 1889, 22, 186. Winkler, *Ber.*, 1890, 23, 2652. Vigouroux, *Ann. Chim. Phys.*, 1897, 12, 153. Power, *Nature*, February 3, 1910.

<sup>4</sup> Winkler, *Ber.*, 1890, 23, 2652.

<sup>5</sup> Gattermann, *Ber.*, 1889, 22, 186.

<sup>6</sup> Moissan and Smiles, *Compt. rend.*, 1902, 134, 1552.

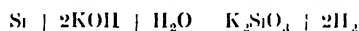
<sup>7</sup> Wigand, *Ann. Phys.*, 1907, 21, 95.

<sup>8</sup> Cambi, *Atti R. Accad. Lincei*, 1911, [v] 20, i, 440.

<sup>9</sup> Wilke-Dorfurt, *Festschrift Otto Wallach*, 1909, 671.

of amorphous silicon exists. The ordinary amorphous silicon can easily be melted in a muffle furnace, and vapourised in the electric furnace, yielding a polyatomic vapour.<sup>1</sup> It readily dissolves in many molten metals; with some, such as magnesium, copper, iron, and nickel, it forms silicides; from others, such as aluminium, it separates in the crystalline state on cooling. It burns with difficulty in air, but brilliantly in oxygen at a red heat, forming silica. The heat of combustion of amorphous silicon was found by von Wartenberg<sup>2</sup> to be 195,000 calories. Previously recorded values are 184,500 calories by Berthelot and 191,000 calories by Mxer.<sup>3</sup> It combines with gaseous fluorine at ordinary temperature, forming the tetrafluoride  $\text{SiF}_4$ ; and with chlorine at 150° C., bromine at 500° C. and iodine at a still higher temperature, in each case to form the tetrahalide. Silicon combines with sulphur at 600° C., with nitrogen at 1600° C., and with boron, carbon, titanium, and zirconium in the electric furnace. Gaseous and liquid hydrogen fluoride easily dissolve silicon, but hydrogen chloride, bromide, and iodide have little action on it even at a red heat. Steam reacts slowly with silicon at a red heat, forming silica and hydrogen. Most oxides are reduced by silicon at high temperature, the affinity of this element for oxygen exceeding that of all other elements except the alkali and alkaline earth metals and boron and aluminium.

All aqueous acids, except a mixture of hydrofluoric and nitric acids, are without action on silicon, but fused alkali and aqueous solutions of alkali dissolve it with evolution of hydrogen, thus:



When silicon is fused with sodium carbonate, silicate is formed and carbon monoxide evolved. Fused potassium dichromate, chlorate, and nitrate oxidise silicon, but a mixture of potassium chlorate and fuming nitric acid has no action upon it (*cf.* carbon).

**Crystalline Silicon.** *Preparation.* Silicon assumes the crystalline form under favourable conditions. Thus it may crystallise from a state of solution in metals, from a state of fusion, or from the condition of vapour.

(1) Crystallised silicon was first obtained by Deville<sup>4</sup> in 1854, during the production of aluminium by the electrolysis of fused sodium aluminium chloride containing silicon as an impurity. The silicon crystallised from the aluminium, and remained behind when the metal was dissolved in hydrochloric acid, just as graphite remains when cast iron is similarly treated.

(2) Wohler<sup>5</sup> obtained crystallised silicon in a similar way, and also devised the following method for the preparation of this substance in quantity. 1 part of aluminium was fused with 20 parts of sodium silicofluoride for fifteen minutes in a Hessian crucible; and the product, when cold, was treated with hydrochloric and hydrofluoric acids, which dissolved the aluminium and sodium fluorides, leaving the silicon behind. Vigouroux<sup>6</sup> modified this method by heating a mixture of 40 grams of aluminium and 125 grams of potassium silicofluoride for

<sup>1</sup> Von Wartenberg, *Zeitsch. Elektrochem.*, 1912, 18, 658.

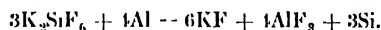
<sup>2</sup> Von Wartenberg, *Festschrift W. Nernst*, 1912, 459.

<sup>3</sup> Deville, *Ann. Chim. Phys.*, 1855, [iii], 43, 27.

<sup>4</sup> Wohler, *Annalen*, 1856, 97, 266, 1857, 102, 382.

<sup>5</sup> Vigouroux, *Ann. Chim. Phys.*, 1897, [vi], 12, 55.

half an hour in an iron crucible to a bright red heat. In this way about 50 grams of silicon were obtained after treatment with acids :



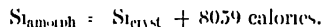
(3) Deville and Caron<sup>1</sup> adopted a modification of Wohler's method. They heated together 3 parts of potassium silicofluoride, 1 part of sodium, and 1 part of granulated zinc to a temperature just below the boiling-point of zinc. The silicon remained after treatment with acid, having crystallised from the molten zinc.

(4) A further method of Vigouxiux consists in heating powdered quartz with excess of aluminium in an electric furnace. Some of the aluminium reduces the silica, and the remainder dissolves the silicon.

(5) Silicon is obtained crystallised from aluminium, when the vapour of silicon tetrachloride is passed over the molten metal. No combination takes place between aluminium and silicon.<sup>2</sup>

All the above methods for obtaining crystallised silicon depend on the crystallisation of this substance from molten aluminium or zinc. Further methods are as follow

(6) Crystallised silicon is formed by fusing the amorphous variety, and allowing the mass to cool. The allotropic change from amorphous to crystalline silicon is accompanied by the evolution of heat<sup>3</sup> in accordance with the equation



According to von Wartenberg,<sup>4</sup> however, the heat evolved is less than two thousand calories.

(7) Crystalline silicon is also formed by sublimation, and was obtained by Moissan during the distillation of silica contained in a graphite crucible heated in an electric furnace.

It is formed in the same way when the vapour of silicon tetrachloride is passed through a heated porcelain tube containing amorphous silicon. In this case the sublimation appears to be due to the formation and decomposition of a lower chloride.

(8) Silicon is also obtained in small, hard crystals when the tetrachloride in presence of hydrogen is decomposed by a carbon rod heated electrically to a high temperature.<sup>5</sup>

(9) Crystallised silicon is prepared according to the method of Kuhne,<sup>6</sup> when a mixture of powdered quartz, aluminium turnings, and sulphur is heated. Water hydrolyses the resulting aluminium sulphide, and sets free the silicon.

(10) Finally, crystalline silicon is produced on a large scale when silica and carbon are heated together in an electric furnace,<sup>7</sup> the carbon being present in quantity insufficient to form carborundum.

When silicon crystallises from molten silver, some of it is in a form which differs from the rest in density (2.42) and in being soluble in

<sup>1</sup> Deville and Caron, *Ann. Chim. Phys.*, 1861, [m], 63, 26, 1863, 67, 435.

<sup>2</sup> Krieser, *Chem. Zeit.*, 1908, 32, 1161.

<sup>3</sup> Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [v], 9, 76.

<sup>4</sup> Von Wartenberg, *Festschrift W. Nernst*, 1912, p. 459.

<sup>5</sup> Pring and Fieding, *Trans. Chem. Soc.*, 1909, 95, 1501.

<sup>6</sup> Kuhne, *German Patent No.* 147,871.

<sup>7</sup> Scheid, *British Patent No.* 18,659 (1899).

hydrofluoric acid.<sup>1</sup> It is regarded by the discoverers as a new allotropic form.

*Properties of Crystalline Silicon.* - Crystalline silicon is light orange in colour and transparent when the crystals are small but generally appears either in black, shining, and metallic-looking six-sided plates which resemble graphite, and are called graphitoidal silicon, or in long needles, known as adamantine silicon. Both kinds of crystals are composed of regular octahedra. Crystallised silicon has a hardness of 7 on Moh's scale and scratches glass; its density is 2.19.<sup>2</sup> The specific heat of crystalline silicon increases with temperature. At 181° C it is only 0.0876,<sup>3</sup> at -- 10° C, it is 0.136, and at 22° C, 0.1697. The gradient of rise becomes less at higher temperature, and above 200° C almost disappears, so that at about 232° C the specific heat becomes constant<sup>4</sup> and equal to 0.203, which gives a value for the atomic heat 5.75. Crystalline silicon resembles graphite in its power to conduct electricity. The spectrum of silicon contains a large number of lines, the chief of which occur in the ultra-violet.<sup>5</sup>

The most intense lines in the spectrum of silicon are as follow<sup>6</sup>

Are : 2507.01, 2516.20, 2521.22, 2528.60, 2881.70, 3905.70.

Spark : 2516.26, 2528.60, 2881.73.

The lines asterisked are also the most persistent, *i.e.* the ultimate lines in the spark spectrum of silicon.<sup>7</sup>

In chemical properties crystalline differs from amorphous silicon in being less reactive; otherwise it is capable of similar reactions. With most of the metals except those of the alkalis silicides are formed; zinc, aluminium, tin, lead, cadmium, gold, silver, and mercury dissolve silicon in quantities which increase with temperature, so that they form crystallising media for this element. The solubility of silicon in zinc, lead, and silver has been studied by Moissan and Siemens.<sup>8</sup>

## ATOMIC WEIGHT OF SILICON

Two distinct considerations generally have to be taken into account in determining the atomic weight of a solid element: (i) a decision has to be made as to the order of magnitude of the atomic weight; (ii) an exact estimation of the chemical equivalent of the element must be carried out by the employment of a suitable chemical reaction.

In the earlier days of atomic-weight determination the values obtained were often erroneous, both from ignorance of the physical laws which have to be taken into account, and from inadequate methods of chemical analysis. This applies particularly to the element silicon; and in tracing the history of the determination of the atomic weight of this element the development of our knowledge of physical methods

<sup>1</sup> Moissan and Siemens, *Compt. rend.*, 1901, 138, 1299.

<sup>2</sup> Wohler, *Annalen*, 1856, 97, 266.

<sup>3</sup> Forch and Nordmeyer, *Ann. Physik*, 1906, 20, 423. See this series, vol. ii, p. 90.

<sup>4</sup> Weber, *Pogg. Annalen*, 1874, 154, 353.

<sup>5</sup> Porlezza, *Gazzetta* 1912, 42, ii, 12, McLennan and Edwards, *Phil. Mag.*, 1915, [vi], 30, 482.

<sup>6</sup> Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

<sup>7</sup> Pollok and Leonard, *Sci. Proc. Roy. Publ. Soc.*, 1907, 8, ix, 217.

<sup>8</sup> Moissan and Siemens, *Compt. rend.*, 1901, 138, 657, 1299, *Ber.*, 1901, 37, 2086.

that indicate the order of magnitude of its value will first be noticed, and then the chemical methods by which this value is determined with exactness.

I. *The Order of Magnitude of the Atomic Weight.*—Various formulæ have been applied at different times to silica and its derivatives.

Thus Berzelius attempted to establish an analogy between potash alum and felspar, so that silica was written  $\text{SiO}_3$  to agree with  $\text{SO}_3$ , the formula then given to sulphuric acid. Dumas<sup>1</sup> in 1826 determined the vapour density of silicon chloride to be 5.94 (air = 1), which, when properly interpreted according to Avogadro's theory, would give a molecular weight of 171.7. Thence it might have been concluded that the chloride could not contain more than 4 atoms of chlorine. Nevertheless, this conclusion was overlooked, and the formula  $\text{SiCl}_6$  was attributed to the chloride to agree with the formula  $\text{SiO}_3$  for the oxide, to which the atomic weight  $\text{Si} = 14.4$  corresponded. No fixed guiding principle had yet been established, however, and the formulæ  $\text{SiO}$  and  $\text{SiCl}_2$ , with  $\text{Si} = 14.8$ , were adopted by Gmelin in 1826. In 1837 Kuhn advocated the formula  $\text{SiO}_2$ , which also found favour with mineralogists.

At different times during the course of about thirty years the formulæ  $\text{SiO}$ ,  $\text{Si}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{SiO}_3$  were in vogue, with the corresponding atomic weights of silicon of approximately 14, 21, 28, and 12, and this uncertainty existed not so much because adequate physical principles for atomic-weight determination had not been discovered as because these principles were misunderstood and perverted.

Gradually, however, a mass of evidence accumulated in favour of the formula  $\text{SiO}_2$  and an atomic weight of 28.

II. Rose showed that the weight of silica which displaces  $\text{CO}_2$  from alkali carbonates at high temperature corresponds with the formula  $\text{SiO}_2$ , and Margnac<sup>2</sup> found that the isomorphism of fluosilicates with fluostannates supported the same formula, although the evidence of Dulong and Petit's law was inconclusive on account of the variation of specific heat with allotropy.

In 1859 Margnac<sup>3</sup> extended the evidence in favour of the formula  $\text{SiO}_2$  by showing the isomorphism of fluotitanates and fluozirconates with fluostannates and fluosilicates; and with the advent of the periodic law silicon found a place in the fourth group with carbon, titanium, zirconium, and tin. Thus an atomic weight of approximately 28 became definitely established for silicon.

The physical evidence for the atomic weight of silicon may thus be summarised:

(1) *Avogadro's Theory.*—When the molecular proportion of any volatile silicon compound, as indicated by vapour-density determination, is analysed, 28 is the smallest proportion of silicon ever found within it.

(2) *Dulong and Petit's Law.*—The atomic heat of silicon reaches the value 5.7 at  $232^\circ \text{C}$ . if the atomic weight is 28; and this is a normal value as compared with analogous elements.<sup>4</sup>

(3) *The Law of Isomorphism.*—In the complex fluorides of silicon, titanium, zirconium, and tin, 28 parts of silicon occupy the place of atomic proportions of the other elements.

<sup>1</sup> Dumas *Ann. Chim. Phys.*, 1826, [ii], 33, 368.

<sup>2</sup> Stagnac, *Œuvres Complètes*, 1858, i, 579-589.

<sup>3</sup> Margnac, *Ann. des Mines*, 1859, [v], 15, 221.

<sup>4</sup> See this series, vol. i, p. 90.

(4) *The Periodic Law*.—The atomic-weight value 28 enables silicon to be placed in the fourth group between aluminum and phosphorus, following carbon, and followed by titanium, zirconium, tin, lead, etc. This position is particularly suitable for an element exhibiting the properties possessed by silicon.

II. *The Exact Value of the Atomic Weight*.—The first attempts to determine the atomic weight of silicon by chemical methods were made by Berzelius<sup>1</sup> and Stromeyer,<sup>2</sup> and were very imperfect.

The work of Pelouze<sup>3</sup> in 1815 marked an advance on former methods. This chemist decomposed silicon tetrachloride with water, and estimated the chlorine by titration with silver nitrate. From his results the value 28.37 for the atomic weight of silicon is deducible, using modern antecedent data.<sup>4</sup>

Dumas<sup>5</sup> in 1859 adopted a similar method which yielded the value 28.08, whilst Schuel<sup>6</sup> two years later employed the same reaction, but weighed the silver chloride. His results lead to the figure 27.95.

The above researches, however, are now merely of historical value. In 1887 Thorpe and Young<sup>7</sup> hydrolysed carefully purified silicon tetrabromide and weighed the silica obtained from it. They found the ratio

$$\text{SiBr}_4 : \text{SiO}_2 = 100 : 17.317$$

whence  $\text{Si} = 28.375$ .

Finally, in 1905, W. Becker and Julius Meyer<sup>8</sup> treated very pure silicon tetrachloride in an analogous manner to the above and obtained gelatinous silica therefrom, which was ignited and weighed as  $\text{SiO}_2$ . They found the ratio

$$\text{SiCl}_4 : \text{SiO}_2 = 100 : 35.115$$

whence  $\text{Si} = 28.225$ .

So far as present knowledge goes there is nothing to choose between these two modern values. Hence the atomic weight of silicon is accepted by the International Atomic Weights Committee to be their mean, namely:

$$\text{Si} = 28.3.$$

It must be remembered, however, that the accumulated evidence for this figure is singularly slight, and that it cannot be regarded as certain even to the first decimal place.

<sup>1</sup> Berzelius, *Göteborgs Annalen*, 1810, 36, 89; 1812, 40, 265; *Schweigger's J.*, 1818, 23, 285; *Pogg. Annalen*, 1826, 8, 20.

<sup>2</sup> Stromeyer, *Göteborgs Annalen*, 1814, 37, 335; 38, 529.

<sup>3</sup> Pelouze, *Compt. rend.*, 1815, 20, 1017.

<sup>4</sup> In calculating these and succeeding data the following values for the fundamental atomic weights have been used: O = 16.000, Cl = 35.457, Br = 79.916, Ag = 107.880.

<sup>5</sup> Dumas, *Ann. Chim. Phys.*, 1859, [iii], 55, 129.

<sup>6</sup> Schuel, *Annalen*, 1861, 120, 91.

<sup>7</sup> Thorpe and Young, *Trans. Chem. Soc.*, 1887, 71, 776.

<sup>8</sup> Becker and Meyer, *Zeitsch. anorg. Chem.*, 1905, 43, 251.

## COMPOUNDS OF SILICON

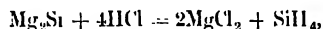
## HYDRIDES OF SILICON

In no respect does silicon differ more widely from carbon than in the number and properties of its hydrides.

To methane and ethane there correspond silico-methane or silicane,  $\text{SiH}_4$ , and silico-ethane,  $\text{Si}_2\text{H}_6$ ; and besides these there probably exist silico-ethylene,  $\text{Si}_2\text{H}_4$ ,<sup>1</sup> the hydrosilicon  $(\text{Si}_2\text{H}_5)_n$  and so-called silico-acetylene,  $(\text{Si}_2\text{H}_2)_n$ , which, however, does not resemble acetylene.

Silicane and silico-ethane bear little resemblance in properties to methane and ethane, and no close relationships appear to exist between their oxy-derivatives. A number of substitution products of these hydrides containing aliphatic or aromatic radicles have, however, been prepared; and these throw light upon the potentialities of the silicon atom. The most important fact established in these researches is that the space-disposition of the valencies of silicon resembles that of carbon, so that optically active "asymmetric" silicon compounds exist.<sup>2</sup>

**Silicon Tetrahydride** (*Silicomethane, Silicane*),  $\text{SiH}_4$ .—Silicon tetrahydride was first obtained, in an impure state, by Buff and Wohler,<sup>3</sup> in 1857, during the electrolysis of a solution of common salt by means of aluminum electrodes containing silicon, and also by the action of dilute hydrochloric acid on magnesium silicide, prepared by fusing together anhydrous magnesium chloride, sodium silicofluoride, common salt, and sodium. The magnesium silicide was more simply prepared by Gattermann,<sup>4</sup> by heating magnesium with sand. The gas obtained in this way, by the reaction



is impure, being mixed with hydrogen and another product, probably another hydride of silicon, which renders it spontaneously inflammable. According to Adwentowski and Drozdowski,<sup>5</sup> however, pure silicane is spontaneously inflammable. The same spontaneously inflammable gas is sometimes observed when a porcelain crucible in which magnesium ribbon has been burnt is cleansed with acid, since the stain on the crucible is magnesium silicide.

According to Moissan and Smiles,<sup>6</sup> the gas evolved by the action of hydrochloric acid on the product formed by heating magnesium and silicon together in the proportion  $\text{Mg} : 2\text{Si}$  is hydrogen mixed with about 5 per cent. of silicon hydrides. These may be separated from hydrogen by cooling them in liquid air, so that they solidify. If the solid hydrides are then allowed to liquefy and volatilise fractionally, silicane is obtained as a gas and silico-ethane remains behind as a liquid.

Silicane can also be obtained mixed with silico-ethane, when silicon

<sup>1</sup> Lebeau, *Compt. rend.*, 1909, 148, 43; see also Desson, *Compt. rend.*, 1912, 154, 1603.

<sup>2</sup> Kipping, *Trans. Chem. Soc.*, 1907, 91, 209.

<sup>3</sup> Buff and Wohler, *Annalen*, 1857, 103, 218, 1858, 106, 56.

<sup>4</sup> Gattermann, *Ber.*, 1889, 22, 186.

<sup>5</sup> Adwentowski and Drozdowski, *Bull. Acad. Sci. Cracow*, 1911, A, 330.

<sup>6</sup> Moissan and Smiles, *Compt. rend.*, 1902, 134, 569.

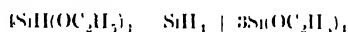
tetrafluoride is passed over heated magnesium, and the solid product is decomposed by acid.<sup>1</sup>

Pure silicane can be prepared by the method of Friedel and Ladenburg,<sup>2</sup> by heating ethyl orthosilicoformate with sodium, though the function of the sodium is unknown.

Ethyl orthosilicoformate is prepared by the interaction of silicochloroform and sodium ethoxide thus



and yields silicane together with ethyl orthosilicate, by a reaction which recalls the behaviour of phosphorous and hypophosphorous acids and their salts when heated, thus

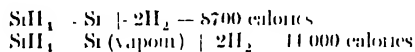


*Properties of Silicane*—Silicane,  $\text{SiH}_4$ , is a colourless gas which when pure is not spontaneously inflammable, but catches fire in contact with a heated knife-blade or hot mercury. It is condensed to a liquid under the following conditions<sup>3</sup>:

Temperature (°C)	-1	7°	11
Pressure (atmospheres)	100	70	50

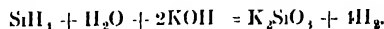
its critical temperature being about 0°C. and its boiling-point<sup>4</sup> - 115°C. to - 116°C. under 730 mm. pressure. According to more recent work,<sup>5</sup> however, its critical temperature is - 3.5°C. and critical pressure 47.8 atmospheres; it solidifies at - 200°C.

Silicane is decomposed into its elements above 400°C., yielding twice its volume of hydrogen, and when it is passed through a red hot tube a mirror of finely divided amorphous silicon is deposited. Its thermochemistry is as follows<sup>6</sup>:



It is also decomposed by electric sparks, but in this case only a part of the hydrogen is set free, and the yellow solid hydride ( $\text{Si}_2\text{H}_6$ )<sub>n</sub> is formed which burns when heated in air or in chlorine.<sup>7</sup>

Silicane takes fire in chlorine gas, producing the tetrachloride  $\text{SiCl}_4$ , and hydrogen chloride, chlorides which easily part with chlorine, such as carbonyl chloride,  $\text{COCl}_2$ , antimony pentachloride,  $\text{SbCl}_5$ , and tin tetrachloride,  $\text{SnCl}_4$ , react similarly with silicane. Silicane burns in oxygen or air, producing silica and water; if cold porcelain is depressed upon the flame, amorphous silicon is deposited upon it. Acids do not decompose silicane, but this gas reacts vigorously with caustic potash solution producing potassium metasilicate and hydrogen, thus



By this means silicane may be estimated.

<sup>1</sup> Warren, *Chem. News*, 1888, 58, 210

<sup>2</sup> Friedel and Ladenburg, *Annalen*, 1867, 143, 126

<sup>3</sup> Ogier, *Compt. rend.*, 1879, 88, 236

<sup>4</sup> Dufour, *Compt. rend.*, 1901, 138, 1010

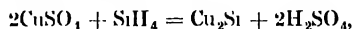
<sup>5</sup> Adwentowski and Drozdowski *Bull. Acad. Sci. Cracovie*, 1911, A, 330

<sup>6</sup> Von Wartenberg, *Zeitsch. anorg. Chem.* 1912, 79, 71

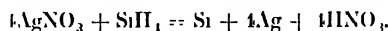
<sup>7</sup> Ogier, *Compt. rend.*, 1879, 89, 1068



This reaction, as well as the ease with which silicane is decomposed by heat, shows the contrast in properties between this substance and methane, from which it is further distinguished by reacting with certain metallic salt solutions. Thus with copper sulphate solution silicane produces chiefly copper silicide, thus :



together with some metallic copper ; but with the more reducible silver nitrate the product consists chiefly of metallic silver mixed with silicon :



In these reactions silicane is comparable with the hydrides of sulphur and arsenic.

**Silico-ethane,  $\text{Si}_2\text{H}_6$ .**—Silico-ethane was discovered by Moissan and Smiles<sup>1</sup> among the products of the action of hydrochloric acid on magnesium silicide, formed by heating magnesium and silicon together in the proportion  $2\text{Mg} : \text{Si}$ . The gas obtained consists of a mixture of hydrogen, silicane, and silico-ethane. The two latter gases were separated from the hydrogen by solidification in tubes surrounded by liquid air ; the silicane was removed from the tubes by fractional vaporisation, leaving the silico-ethane behind.

Silico-ethane may also be prepared from lithium silicide,<sup>2</sup> which has the corresponding composition,  $\text{Si}_2\text{Li}_6$ , by decomposing it with concentrated hydrochloric acid.

Silico-ethane is a mobile, colourless liquid, heavier than, and sparingly soluble in, water. It boils at  $52^\circ \text{C}$ .<sup>3</sup> or, according to Lebeau,<sup>1</sup> at  $-7^\circ \text{C}$ ., and after solidification by means of liquid air, melts at  $-138^\circ \text{C}$ . Its vapour may be heated to  $100^\circ \text{C}$ . without decomposition, at which temperature the density is found to be 2.37 (air = 1), whilst silico-ethane requires 2.41. It is decomposed into its elements at  $240^\circ \text{C}$ ., and electric sparks decompose it, separating amorphous silicon.

Silico-ethane takes fire spontaneously and even explosively in the air, burning to silica and water ; drying with sulphuric acid increases the vigour of the reaction ; it precipitates the metals from aqueous solutions of mercuric chloride, auric chloride, and silver nitrate ; potassium dichromate and permanganate solutions, as well as bromine water, oxidise it to silicic acid. Carbon tetrachloride and sulphur hexafluoride react explosively with silico-ethane, with formation of the halogen hydrides and separation of the solid elements. Silico-ethane reacts with caustic potash solution similarly to silicane ; in this way one molecule produces seven molecules of hydrogen :



and the volume of hydrogen evolved serves to estimate the substance.

It appears from these reactions that silico-ethane resembles silicane in chemical properties, and differs entirely from ethane. There is no reason to suppose it differs from this hydrocarbon in constitution, but there are two reasons why it has different properties. For not only does it easily lose hydrogen, a property it shares with silicane, but

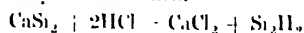
<sup>1</sup> Moissan and Smiles, *Compt. rend.*, 1902, **134**, 569, 1549.

<sup>2</sup> Moissan, *Compt. rend.*, 1902, **134**, 1083 ; 1903, **135**, 1284.

<sup>3</sup> Lebeau, *Compt. rend.*, 1909, **148**, 43, *Bull. Soc. chim.*, 1909, [iv], 5, 89.

the two silicon atoms permit of oxygen intervening between them in the process of oxidation.

**Silico-acetylene**,  $(\text{Si}_2\text{H}_2)_n$ , was prepared by Bradley<sup>1</sup> by decomposing calcium silicide with hydrochloric acid



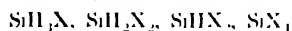
It is a yellow crystalline substance, showing no resemblance to acetylene, and is undoubtedly polymerised.

The following table shows the boiling- and melting-points of the three hydrides of silicon, together with those of the corresponding hydrocarbons. The difference in boiling-point between ethane and silico-ethane is particularly noteworthy.

	$\text{CH}_4$	$\text{SiH}_4$	$\text{C}_2\text{H}_6$	$\text{Si}_2\text{H}_6$	$\text{C}_2\text{H}_4$	$(\text{Si}_2\text{H}_2)_n$
B.P. °C.	-164	-115	-93	-12	sublimation	solid
M.P. °C.	-184	-200	-123	-138	temperature	M.P.
					So	unknown

#### SILICON AND THE HALOGENS

Various silicon compounds exist in which the hydrogen atoms of silane appear successively replaced by halogen atoms, as in the series:



Of these compounds all the four tetrahalides are known, as well as all the compounds of the type  $\text{SiHX}_3$ ; only isolated examples of  $\text{SiH}_2\text{X}_2$  and  $\text{SiH}_3\text{X}$ , however, exist.

The tetrahalides,  $\text{SiX}_4$ , are the halides of orthosilicic acid,  $\text{Si}(\text{OH})_4$ , which all of them produce, together with halogen hydric acid, when they are hydrolysed by water. Silicon tetrafluoride, however, differs from the other halides in not suffering complete hydrolysis, but giving rise, instead, to the complex acid  $\text{H}_2\text{SiF}_6$ . A noteworthy characteristic of silicon is its power to form mixed halides containing two kinds of halogen atoms, selected from chlorine, bromine, and iodine. A complete series of these compounds exists.

Of halides containing more than one silicon atom there are known the chloride, bromide, and iodide of the type  $\text{Si}_2\text{X}_6$ , also the chlorides and bromides  $\text{Si}_3\text{X}_8$  and  $\text{Si}_3\text{X}_{10}$ , and the chlorides  $\text{Si}_4\text{Cl}_{12}$  and  $\text{Si}_6\text{Cl}_{18}$ .

Thus it appears that silicon possesses a greater power of forming halides than hydrides containing more than one silicon atom.

The table on page 188 contains a list of all these compounds, with their boiling- and melting-points.

The compounds will be considered in the order in which they are placed in the table.

**Bromosilicane**,  $\text{SiH}_3\text{Br}$ , boiling at  $30^\circ$ – $40^\circ\text{C}$ ., and **Dibromosilicane**,  $\text{SiH}_2\text{Br}_2$ , boiling at  $75^\circ\text{C}$ ., are liquids<sup>2</sup> produced together with silico-bromoform when hydrogen bromide acts on silicon. They are the sole representatives of their class, and little is known about them.

<sup>1</sup> Bradley, *Chemical News*, 1900, 82, 149.

<sup>2</sup> Besson and Fournier, *Compt. rend.*, 1910, 151, 1055.

Name	Formula	Boiling-point °C	Melting-point °C
Bromosilicane . . .	SiH <sub>3</sub> Br	30°-40	—
Dibromosilicane . . .	SiH <sub>2</sub> Br <sub>2</sub>	75°	—
Silicofluoroform . . .	SiHF <sub>3</sub>	80	— 110
Silicochloroform . . .	SiHCl <sub>3</sub>	33	— 131°
Silicobromoform . . .	SiHBr <sub>3</sub>	100°-111	below - 60
Silicoiodoform . . .	SiHI <sub>3</sub>	106-11 mm	+ 8°
Silicon tetrafluoride . .	SiF <sub>4</sub>	65	— 77°
Hydrofluosilic acid	H <sub>2</sub> SiF <sub>6</sub>		
Silicon tetrachloride	SiCl <sub>4</sub>	59.6	— 89°
Silicon tetrabromide	SiBr <sub>4</sub>	150.8	5°
Silicon tetraiodide	SiI <sub>4</sub>	120.5°	290°
Bromotrichlorosilicane	SiCl <sub>3</sub> Br	80	—
Dibromodichlorosilicane	SiCl <sub>2</sub> Br <sub>2</sub>	100 or 103-105	—
Tribromochlorosilicane	SiClBr <sub>3</sub>	126-128 or 110-111	— 39°
Iodotrichlorosilicane	SiCl <sub>3</sub> I	113-114	—
Diiododichlorosilicane	SiCl <sub>2</sub> I <sub>2</sub>	172	—
Triiodochlorosilicane	SiClI <sub>3</sub>	234-237	2°
Iodotribromosilicane	SiBr <sub>3</sub> I	192	14°
Diiododibromosilicane	SiBr <sub>2</sub> I <sub>2</sub>	230-231	38°
Triiodobromosilicane	SiBrI <sub>3</sub>	250	54°
Hexachlorosilicoethane	Si <sub>2</sub> Cl <sub>6</sub>	146-148	1°
Hexabromosilicoethane	Si <sub>2</sub> Br <sub>6</sub>	265°	95°
Hexaiodosilicoethane	Si <sub>2</sub> I <sub>6</sub>		250°
Octachlorosilicopropane	Si <sub>3</sub> Cl <sub>8</sub>	215-218	— 67°
Octabromosilicopropane	Si <sub>3</sub> Br <sub>8</sub>		133
Decachlorosilicobutane	Si <sub>4</sub> Cl <sub>10</sub>	149-151-15 mm	
Decabromosilicobutane	Si <sub>4</sub> Br <sub>10</sub>		185
Dodecachlorosilicopentane	Si <sub>5</sub> Cl <sub>12</sub>	190°/15 mm	—
Tetradecachlorosilicohexane	Si <sub>6</sub> Cl <sub>14</sub>		170

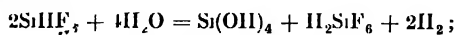
**Silicofluoroform** (*Trifluorosilicane*), SiHF<sub>3</sub>.—The other three compounds of the type SiHX<sub>3</sub> are formed by the action of the halogen hydrazide on silicon; silicofluoroform, however, has not been prepared in this way, but is derived from silicochloroform by the replacement of its chlorine by fluorine. This may be done by heating the latter substance to 220° C. with tin tetrafluoride or to 100-120° C. if titanium tetrafluoride is employed:



The operation is carried out in a sealed copper flask or gun-barrel; and silicofluoroform is formed as a colourless gas which on strong cooling condenses to a liquid boiling at - 80° C., from which a crystalline solid melting at - 110° C. can be obtained. The vapour density of silico-fluoroform (n = 1) has been found to be 3.02, the theoretical value being 2.99.<sup>1</sup>

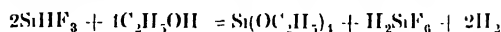
Gaseous silicofluoroform is not very stable, but decomposes, slowly at atmospheric temperature, quickly on heating to 120° C. in accordance with the reaction:  $4\text{SiHF}_3 = 3\text{SiF}_4 + 2\text{H}_2 + \text{Si}$ .

It burns with a bluish flame, producing amorphous silicic acid, and forms an explosive mixture with air. Water and dilute alkalis decompose the gas thus:

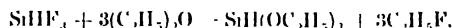


<sup>1</sup> Ruft and Albert, *Ber.*, 1905, 38, 53

absolute alcohol produces, similarly, ethylorthosilicate :



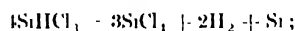
(*cf.* reaction with silicochloroform), while ether yields the ester of the corresponding acid, orthosilicic formic acid :



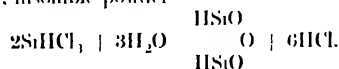
**Silicochloroform** (*Trichlorosilicane*),  $\text{SiHCl}_3$ . Silicochloroform, so named because of its analogy with chloroform, was obtained impure by Buff and Wohler<sup>1</sup> in 1857 by heating silicon in a current of dry hydrogen chloride gas, and was examined later by Friedel and Ladenburg.<sup>2</sup> Gattermann<sup>3</sup> showed that it could be obtained in the same way from the crude silicon formed by heating silica with magnesium; it must, however, be freed from the tetrachloride formed at the same time by fractional distillation, and then be condensed in a freezing mixture. Ferrosilicon and copper silicide may be employed in place of silicon itself.

Silicochloroform is a colourless, mobile, strongly smelling liquid which boils at 33° C. under 758 mm. pressure<sup>4</sup> and forms a crystalline solid which melts at -131° C. The density of the liquid at 15° C. is 1.3138, and its vapour density 1.61, which corresponds with theory. It may be observed that chloroform,  $\text{CHCl}_3$ , boils at 61.5° C. It will be noticed in the course of what follows that, apart from polymerisation, silicon compounds are generally more volatile than the corresponding carbon compounds.

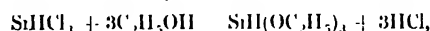
When silicochloroform is heated in an indifferent atmosphere it decomposes similarly to silicofluoroform, thus :



its vapour burns in the air with a green-mantled flame, like that of chloroform, producing clouds of silica, and forms with air a mixture which can be exploded by means of a hot glass rod. Unlike chloroform and carbon tetrachloride, but like silicon tetrachloride, silicochloroform fumes in moist air, and is decomposed by water, with evolution of heat, forming silica and hydrochloric acids. If, however, the reaction takes place at 0° C. the hydrogen is retained, and silicic formic anhydride is produced as a white, insoluble powder :



Alcohol reacts normally, producing ethyl orthosilicoformate :



and not ethyl orthosilicate, as with silicofluoroform.

**Silicobromoform** (*Tribromosilicane*),  $\text{SiHBr}_3$ , is formed similarly to silicochloroform by the action of hydrogen bromide on crude silicon prepared from silica and magnesium,<sup>5</sup> and is freed from the tetrabromide by fractional distillation. Silicobromoform is a colourless liquid which

<sup>1</sup> Buff and Wohler, *Annalen*, 1857, 104, 91.

<sup>2</sup> Friedel and Ladenburg, *Compt. rend.*, 1867, 64, 359.

<sup>3</sup> Gattermann, *Ber.*, 1889, 22, 190.

<sup>4</sup> Ruff and Albert, *Ber.*, 1905, 38, 53.

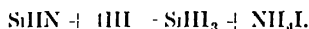
<sup>5</sup> Buff and Wohler, *Annalen*, 1857, 104, 99.

boils at 115°–117° C. (Gattermann <sup>1</sup>) or 109°–111° C. (Besson <sup>2</sup>) ( $\text{CIBr}_3$  boils at 151° C.); it does not solidify at – 60° C.

Its vapour ignites spontaneously in the air; and the liquid reacts with water, forming, when kept cool, silicoformic anhydride. Silico-bromoform appears to form additive compounds with ammonia and phosphine.

According to von Mahn <sup>3</sup> *pentabromosilicoethane*,  $\text{Si}_2\text{IBr}_5$ , is formed by the interaction of silicane and bromine, and forms colourless needles which melt at 89° C, the boiling-point of the liquid being 230° C.

**Silico-iodoform** (*Tri-iodosilicane*),  $\text{SiI}_3$ . Silico-iodoform was prepared by Buff and Wohler <sup>4</sup> by the action of hydrogen iodide gas on heated silicon, and the method was improved upon by Friedel, <sup>5</sup> who mixed hydrogen with the hydrogen iodide. Ruff <sup>6</sup> has found that when silicochloroform reacts with ammonia at – 15° C, silicohydrogen hydride,  $\text{SiHN}$ , is formed; and when this is suspended in carbon disulphide and treated with hydrogen iodide at low temperature, silico-iodoform is produced according to the reaction:



The ammonium iodide is filtered off and the silico-iodoform freed from the solvent, carbon disulphide, and from silicon tetra-iodide by distillation. An even better result is obtained by employing aniline instead of ammonia. Silicon hydrotriamide is formed, which reacts with hydrogen iodide thus:



Silico-iodoform is a colourless liquid having a density of 3.286 at 23° C, <sup>6</sup> or 3.314 at 20° C, and 3.362 at 0° C, <sup>6</sup> which solidifies at + 8° C, and distils under reduced pressure as follows:

Pressure mm		Temperature
14	....	106
22	....	111
67	....	132
122	.. .	155

At about 150° C, it begins to decompose, but on further heating some of it can be distilled, and condensed at about 220° C, under atmospheric pressure. Silico-iodoform vapour burns in the air, and the liquid is decomposed by water like the chlorine compound, yielding silicoformic anhydride and hydriodic acid.

**Silicon Tetrafluoride**,  $\text{SiF}_4$ . Silicon tetrafluoride was discovered by Scheele in 1771, obtained independently by Priestley, and examined by Gay Lussac and Thénard (1808), and by J. Davy <sup>7</sup> (1812), but more

<sup>1</sup> Gattermann, *Ber.*, 1889, 22, 193

<sup>2</sup> Besson, *Compt. rend.*, 1891, 112, 530

<sup>3</sup> Von Mahn, *Monat. Zeitsch.*, 1869, 5, 163.

<sup>4</sup> Buff and Wohler, *Annalen*, 1857, 104, 99

<sup>5</sup> Friedel, *Compt. rend.*, 1868, 67, 98.

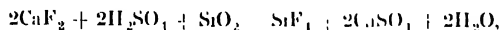
<sup>6</sup> Ruff, *Ber.*, 1908, 41, 3738

<sup>7</sup> Davy, *Phil. Trans.*, 1812, 352

especially by Berzelius<sup>1</sup> (1823). It is usually prepared by the interaction of hydrofluoric acid and silica:



which is carried out by heating together sand, fluor spar, and excess of concentrated sulphuric acid in a flask



the excess of acid being needed to prevent the decomposition of the silicon tetrafluoride by water.

Silicon tetrafluoride, which is evolved as a gas, is then frequently passed into water, with which it undergoes a characteristic reaction, to which reference will be shortly made.

Silicon tetrafluoride was prepared synthetically by Moissan<sup>2</sup>, and, according to Vigouroux<sup>3</sup> amorphous silicon reacts with fluorine with incandescence, forming the tetrafluoride. The pure gas may be conveniently prepared by heating dry barium silicofluoride,<sup>4</sup>  $\text{BaSiF}_6$ , 30–40 grams of which yield 2–3 litres of the gas, which may be collected over mercury. Silicon tetrafluoride may be separated from hydrogen fluoride, occurring with it as it is commonly prepared, by cooling the mixture to  $-60^\circ \text{C}$ , which condenses the latter gas, or by passing the mixed gases through sodium fluoride, which retains hydrogen fluoride.

*Properties of Silicon Tetrafluoride.* Silicon tetrafluoride is a colourless, pungent, fuming gas, which can be liquefied and solidified. The gas solidifies at  $-97^\circ \text{C}$ , under atmospheric pressure, and the solid sublimates again without melting, but melts under 2 atmospheres pressure at  $-77^\circ \text{C}$ , forming a transparent and very mobile liquid, which boils at  $-65^\circ \text{C}$ , under 1810 mm pressure. The critical temperature of silicon tetrafluoride is  $-1.5^\circ \text{C}$  and the critical pressure 50 atmospheres.<sup>5</sup> The density of the gas was found by J. Davy<sup>6</sup> to be 3.5735 and by Dumas<sup>7</sup> 3.6, theory requiring 3.619. Jaquierod and Tourpauan<sup>8</sup> found the weight of a normal litre to be 4.693 grams, but when the gas was passed over glass wool at a red heat the weight was increased to 4.820 grams, which increase the authors attribute to the formation of a subfluoride. The heat of formation of silicon tetrafluoride from crystallised silicon and gaseous fluorine is, according to Guntz<sup>9</sup> 239,800 calories. The gas is not decomposed by electric sparks or the silent electric discharge, but silicon is separated in the electric arc: sodium and potassium burn in the gas, forming fluorides, and certain metallic oxides, e.g. lime, likewise react with silicon tetrafluoride, forming silica and the fluoride of the metal.

The most characteristic reaction of silicon tetrafluoride is that with

<sup>1</sup> Berzelius, *Pogg. Annalen*, 1824, 1, 169.

Moissan, *Ann. Chim. Phys.*, 1887, [vi], 12, 472.

<sup>3</sup> Vigouroux, *Compt. rend.*, 1895, 120, 367.

<sup>4</sup> Trichot, *Compt. rend.*, 1884, 98, 821.

<sup>5</sup> Moissan, *Compt. rend.*, 1901, 139, 711.

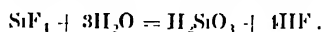
<sup>6</sup> Davy, *Phil. Trans.*, 1812, 352.

<sup>7</sup> Dumas, *Ann. Chim. Phys.*, 1826, [ii], 33, 367.

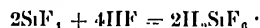
<sup>8</sup> Jaquierod and Tourpauan, *J. Chim. phys.*, 1913, 11, 3.

<sup>9</sup> Guntz, *Ann. Chim. Phys.*, 1884, [vi], 3, 59.

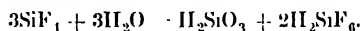
water,<sup>1</sup> by which gelatinous silica and hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) are formed. The first reaction is one of hydrolysis:



but this hydrolysis is not perfect, for silicon tetrafluoride combines with hydrogen fluoride to form hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$ , which can exist in aqueous solution:



consequently the complete reaction is



Hence it will be understood that when silicon tetrafluoride is passed into a concentrated solution of hydrogen fluoride, hydrofluosilicic acid is formed without separation of silicic acid.

Hydrolytic decomposition of silicon tetrafluoride can take place with steam at high temperature, and under these conditions anhydrous crystalline silica may be gradually deposited. Probably this kind of reaction, which is called pneumatolysis, has played some part in the formation of silica minerals.

Dry ammonia combines with silicon tetrafluoride, forming the crystalline compound  $\text{SiF}_4 \cdot 2\text{NH}_3$ ,<sup>2</sup> which is decomposed by water; phosphine forms the compound  $3\text{SiF}_4 \cdot 2\text{PH}_3$ ,<sup>3</sup> at  $-22^\circ \text{C}$  under 50 atmospheres pressure, but this compound is unstable, dissociating into its constituents at ordinary temperature. Silicon tetrafluoride reacts with alcohol,<sup>4</sup> forming ethyl orthosilicate and hydrofluosilicic acid; it also combines with acetone<sup>5</sup> and with organic bases.<sup>6</sup>

**Hydrofluosilicic Acid,  $\text{H}_2\text{SiF}_6$ .**—The remarkable effect of passing silicon tetrafluoride gas into water was observed and commented upon by Priestley.<sup>7</sup> In the reaction



which has already been noticed, the silicic acid separates in the form of "gelatinous silica," having approximately the composition  $(\text{H}_2\text{SiO}_3)_n$ , whilst the hydrofluosilicic acid remains in solution. In consequence of this reaction the delivery tube through which silicon tetrafluoride is passing is not allowed to dip directly into water, but ends beneath the surface of mercury through which the gas passes into water. By this means the blocking of the delivery tube by the gelatinous silica is avoided. When the reaction has proceeded long enough, the gelatinous silica is filtered off and a dilute solution of hydrofluosilicic acid is obtained. A solution of the acid may also be produced by decomposing its calcium salt with sulphuric acid, and by passing silicon tetrafluoride gas into concentrated hydrofluoric acid. A dilute solution may be concentrated by evaporation at low temperature.

<sup>1</sup> Berzelius, *Pogg. Annalen*, 1824, **1**, 169.

<sup>2</sup> Davy, *Phil. Trans.*, 1812, 352.

<sup>3</sup> Besson, *Compt. rend.*, 1890, **110**, 80.

<sup>4</sup> Knop, *J. prakt. Chem.*, 1858, **74**, 41, 1867, **101**, 157.

<sup>5</sup> Norton and Westenholtz, *Amer. Chem. J.*, 1888, **10**, 209.

<sup>6</sup> Comey and Jackson, *Amer. Chem. J.*, 1888, **10**, 165, Comey and Smith, *Amer. Chem. J.*, 1888, **10**, 297.

<sup>7</sup> Vide Thorpe's Essay on Priestley, *Essays in Historical Chemistry* (Macmillan and Co.), 1894, p. 48.

Solutions of hydrofluosilicic acid of different strengths have the following densities at 17.5° C. (water at 17.5° C. = 1.0):

% $\text{H}_2\text{SiF}_6$	Density	% $\text{H}_2\text{SiF}_6$	Density	% $\text{H}_2\text{SiF}_6$	Density
0.5	1.0010	5.0	1.0107	20.0	1.1748
1.0	1.0080	10.0	1.0831	30.0	1.2235
1.5	1.0120	15.0	1.1281	30.0	1.2712
2.0	1.0161				

A concentrated solution of hydrofluosilicic acid is a fuming acid liquid, the molecular conductivities of the acid at different dilutions and 25° C. being, according to Ostwald<sup>2</sup>

$\nu$	$\lambda_{\nu}$	$\nu$	$\lambda_{\nu}$	$\nu$	$\lambda_{\nu}$
2	216	32	371	112	113
4	260	64	442	1024	195
8	281	128	508	2048	652
16	301	256	577	4096	847

The increase in conductivity above  $\nu = 256$  is due to the hydrolysis of hydrofluosilicic acid into silicic and hydrofluoric acids.

A crystalhydrate of the acid,  $\text{H}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$  which melts at 19° C., is deposited from a concentrated solution at low temperature, but the anhydrous acid has never been obtained, for its solution can be evaporated completely, leaving no residue. This is due to the vapourisation of hydrofluosilicic acid together with steam, the hydrofluosilicic acid being partly dissociated into hydrogen fluoride and silicon tetrafluoride. The phenomena observable on the distillation of hydrofluosilicic acid solutions have been studied by Baur and Glaessner.<sup>3</sup> The vapour arising from a 13.3 per cent. solution of the acid has a composition corresponding to that required by the formula  $2\text{HF} \cdot \text{SiF}_4$ , and is partly dissociated, it being estimated from vapour-density determinations that at 100° C. hydrofluosilicic acid vapour is more than two-thirds dissociated. The distillate from an acid more concentrated than 13.3 per cent. contains silicic acid, from which it is inferred that silicon tetrafluoride leaves the solution more rapidly than hydrogen fluoride and then suffers hydrolysis in the distillate, on account of its excess of hydrogen fluoride the remaining acid dissolves silicic acid when evaporated with it. The distillate from an acid weaker than 13.3 per cent. contains excess of hydrogen fluoride, and the residual acid deposits silicic acid on evaporation owing to the hydrolysis of remaining silicon tetrafluoride. It may be added that a solution which will dissolve silicic acid will etch glass, but that a solution containing only hydrofluosilicic acid does not etch glass.

**Salts of Hydrofluosilicic Acid, Fluosilicates, Silicifluorides.**—The salts of this acid are obtained by dissolving metallic oxides or carbonates

<sup>1</sup> Stolba, *J. prakt. Chem.*, 1863, 90, 193.

<sup>2</sup> Ostwald, *J. prakt. Chem.*, 1885, [u], 32, 300.

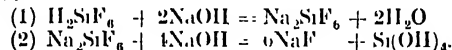
<sup>3</sup> Baur, *Ber.*, 1903, 36, 4209; Baur and Glaessner, *Ber.*, 1903, 36, 4215.



in the aqueous acid, by causing silicon tetrafluoride to act on metallic fluorides in the solid state or in strong solution, by dissolving silicic acid with a metallic fluoride in aqueous hydrofluoric acid, or by precipitation. The salts are crystalline, and are soluble in water except those of the alkali metals and barium. The insolubility of barium silicifluoride—1 part dissolves in 3802 parts of cold water<sup>1</sup>—is sometimes employed as a means of separating this metal in analysis.

Silicifluorides lose silicon tetrafluoride when heated strongly, leaving a residue of fluoride; concentrated sulphuric acid liberates hydrofluosilicic acid, which is evolved, and dissociates on heating.

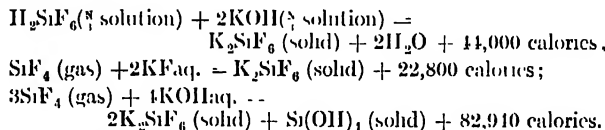
Alkali hydroxide and carbonate solutions decompose a silicifluoride, forming fluoride and silicate. Consequently when a solution of hydrofluosilicic acid is titrated with caustic soda solution in presence of litmus, two transition points are observed corresponding to the neutralisation of the original acid and the decomposition of the resulting silicifluoride, thus:



Litmus shows the permanent excess of alkali after the completion of the second reaction, since  $\text{Si(OH)}_4$  does not behave as an acid towards this indicator.

If excess of ammonia is added to a solution of hydrofluosilicic acid, gelatinous silica gradually separates owing to a similar decomposition.

The silicifluorides are isomorphous with the corresponding titanium and stannic fluorides.<sup>2</sup> The following are thermochemical data relating to the potassium salt<sup>3</sup>:



**Silicon Subfluoride.**—According to Deville<sup>4</sup> and Troost and Hautefeuille<sup>5</sup> a lower fluoride of silicon is formed when gaseous silicon tetrafluoride is passed over silicon heated to the softening-point of glass and then suddenly cooled. A white, volatile powder is thus deposited, which contains less fluorine than silicon tetrafluoride and reduces permanganate solution; it is supposed to be a derivative of ter- or bi-valent silicon.<sup>6</sup>

**Silicon Tetrachloride** (*Tetrachlorosilane*),  $\text{SiCl}_4$ .—Silicon tetrachloride was first obtained by Berzelius<sup>7</sup> in 1823, and is formed by the union of its elements when dry chlorine is passed over heated amorphous or crystalline silicon. Instead of pure silicon the crude product obtained by Gattermann's method may be employed, being heated to 300°–310°C,<sup>8</sup> or magnesium silicide may be gently heated in a combustion tube,

<sup>1</sup> Fieserius, *Annalen*, 1816, 59, 120.

<sup>2</sup> Thus similar nomenclature is justified, see note, p. 176

<sup>3</sup> Truchot, *Compt. rend.*, 1884, 98, 1330.

<sup>4</sup> Deville, *Ann. Chim. Phys.*, 1857, [iii], 49, 76.

<sup>5</sup> Troost and Hautefeuille, *Ann. Chim. Phys.*, 1871, [v], 7, 464.

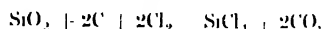
<sup>6</sup> See also Jaqueroi and Tourpau, *J. Chim. phys.*, 1913, ix, 3.

<sup>7</sup> Berzelius, *Pogg. Annalen*, 1824, i, 219.

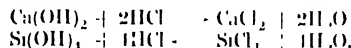
<sup>8</sup> Gattermann and Weinlig, *Ber.*, 1894, 27, 1943.

through which chlorine is passed, and the silicon tetrachloride condensed in a receiver surrounded by ice. The silicon tetrachloride thus prepared will contain some  $\text{Si}_2\text{Cl}_6$  and a little  $\text{SiCl}_3$  from which it is freed by fractional distillation. It may also be obtained by passing chlorine over ferosilicon, containing 15 per cent. of silicon, which is heated to redness in a fire-clay retort, and also similarly from euprosilicon.

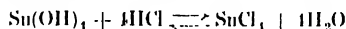
Lastly, silicon tetrachloride may be made by passing chlorine over a heated mixture of silica and carbon.



This reaction is typical of a general method for preparing non-metallic chlorides, and differs essentially from that to be employed for metallic chlorides, viz. the action of hydrochloric acid upon their oxides or hydroxides. Consider, for example, the two reactions



The difference between the metal and the non-metal is signalled by the direction of the reaction. This difference, however, is seldom absolute, and with elements of intermediate character it disappears. In the case of stannic tin, for example, the reaction is reversible



and stannic chloride can be prepared either by dissolving stannic hydroxide in hydrochloric acid, or by passing chlorine over heated tin or a mixture of stannic oxide and carbon.

**Properties of Silicon Tetrachloride.** Silicon tetrachloride is a heavy, colourless, fuming liquid. There is some discrepancy between different observations of its boiling-point, probably owing to the difficulty of obtaining the compound free from higher chlorides. The results lie between  $59^\circ\text{C}$ . and  $56.9^\circ\text{C}$ . at 760 mm. pressure. The latter temperature, observed by J. Meyer and Becker,<sup>1</sup> is probably most nearly correct. This compound solidifies at  $-89^\circ\text{C}$ .

Numerous observations have been made upon the density, the mean of four closely agreeing results<sup>2</sup> being 1.521. Dumas<sup>3</sup> found the vapour density to be 5.9390; Regnault<sup>4</sup> found it to be 5.86, the calculated value being 5.8833. The critical temperature is  $230^\circ\text{C}$ .<sup>5</sup> and the heat of formation 157,640 calories.<sup>6</sup> The vapour is not found to dissociate at the softening-point of porcelain.

Like acid chlorides in general, but unlike carbon tetrachloride, silicon tetrachloride suffers hydrolytic decomposition by water, forming hydrochloric acid, and the acid corresponding to the chloride, in this case silicic acid; consequently, when silicon tetrachloride reacts with water gelatinous silica separates. The heat of this reaction has been measured by Berthelot<sup>7</sup> and Thomsen,<sup>8</sup> who found it to be 69,000 and 69,300 calories per gram-molecule respectively. When steam reacts

<sup>1</sup> J. Meyer and Becker, *Zeitsch. anorg. Chem.*, 1905, 43, 251.

<sup>2</sup> Thorpe, *Trans. Chem. Soc.*, 1880, 37, 327.

<sup>3</sup> Dumas, *Ann. Chim. Phys.*, 1859, [iii], 55, 183.

<sup>4</sup> Regnault, *Compt. rend.*, 1853, 36, 687.

<sup>5</sup> Mendeleeff, *Annalen*, 1861, 119, 11.

<sup>6</sup> Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [v], 9, 70.

<sup>7</sup> Berthelot, *Ann. Chim. Phys.*, 1878, [v], 15, 213.

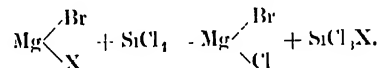
<sup>8</sup> Thomsen, *Ber.*, 1873, 6, 711.

with silicon tetrachloride vapour at a red heat crystallised silica is formed, and if metallic oxides are present crystallised artificial silicates may be prepared. Silicon tetrachloride reacts with dry air at a white heat to form oxychloride; it may be distilled from sodium or potassium, since it does not react with these metals below 200° C., though at a red heat it yields its chlorine to them, amorphous silicon being separated; zinc and silver, and to a less extent copper and iron, react similarly, but in no case is a lower chloride of silicon formed.

Hydrogen sulphide at a red heat forms silicon tetrachlorohydro-sulphide,  $\text{SiCl}_4\text{SiH}_4$ , and hydrogen bromide and iodide effect a change of halogen with the formation of mixed silicon halides (*q.v.*). Phosphoric oxide forms phosphoryl chloride and silica, sulphur trioxide forms pyrosulphuryl chloride,  $\text{S}_2\text{O}_5\text{Cl}_2$ , and concentrated sulphuric acid produces silicic acid with evolution of hydrogen chloride. Silicon tetrachloride also reacts with many metallic oxides, forming silica and metallic chlorides or oxychlorides<sup>1</sup>; with nitrous acid it forms nitrosyl chloride, and it reacts similarly with fatty acids, forming their chlorides, while with alcohol it forms ethyl silicate.<sup>2</sup>

Silicon tetrachloride is the starting-point for the preparation of organic derivatives of silicon, which are now known in large numbers. The chlorine atoms may be exchanged for organic radicals through the agency of (i) zinc alkyls, (ii) sodium and alkyl bromides or iodides<sup>3</sup> (Fittig's reaction), or (iii) by Kipping's application of the more recently discovered and valuable Grignard's reagent, in which magnesium reacts with an alkyl or aryl bromide in ethereal solution, producing

magnesium alkyl or aryl bromide,  $\text{Mg} \begin{smallmatrix} \nearrow \text{Br} \\ \searrow \text{X} \end{smallmatrix}$ , which can then exchange its organic radical for a chlorine atom of silicon tetrachloride,<sup>4</sup> thus:



Besides these substitution products, silicon tetrachloride also forms some addition compounds. It forms with ammonia a white, infusible mass having the composition  $\text{SiCl}_4 \cdot 6\text{NH}_3$ ; and absorbs phosphine at low temperature, forming substances of indefinite composition. Thus at -20° C. silicon tetrachloride absorbs twenty times, and at -50° C. forty times, its volume of hydrogen phosphide. By strong compression at low temperature silicon tetrachloride and hydrogen phosphide can be made to form an unstable crystalline compound<sup>5</sup> whose composition is unknown. Silicon tetrachloride also forms additive compounds with organic bases.<sup>6</sup>

**Silicon Tetrabromide** (*Tetrabromosilicane*),  $\text{SiBr}_4$ .—Silicon tetrabromide, first obtained by Serullas,<sup>7</sup> is prepared similarly to silicon

<sup>1</sup> Rauter, *Annalen*, 1892, 270, 244.

<sup>2</sup> Friedel and Crafts, *Ann. Chim. Phys.*, 1863, [iv], 9, 12.

<sup>3</sup> Kipping, *Trans. Chem. Soc.*, 1901, 79, 450.

<sup>4</sup> Kipping, *Proc. Chem. Soc.*, 1904, 20, 15. *Trans. Chem. Soc.*, 1907, 91, 210. Dilthey, *Ber.*, 1904, 37, 1130.

<sup>5</sup> Bosson, *Compt. rend.* 1890, 110, 240.

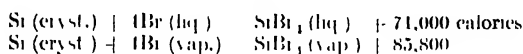
<sup>6</sup> Harden, *Trans. Chem. Soc.*, 1886, 51, 40. Reynolds, *Trans. Chem. Soc.*, 1888, 55, 474.

<sup>7</sup> Serullas, *Ann. Chim. Phys.*, 1831, [ii], 48, 87.

tetrachloride<sup>1</sup> by passing bromine vapour over an intimate mixture of silica and carbon or the crude silicon of Gattermann<sup>2</sup>, hydrogen bromide may be substituted for bromine when silicobromoforn accompanies the tetrabromide. An alternative method consists in causing silicon tetrachloride to react with carbon tetrabromide,<sup>3</sup> when exchange of halogen takes place.

*Properties of Silicon Tetrabromide.* Silicon tetrabromide is a heavy, colourless liquid which evolves dense white fumes in moist air; its density at 0° C. is 2.8128 (Petric) or 2.82 (Reynolds), its boiling-point has been found by different observers to lie between 148° C. and 154° C. The most recent, and probably the most accurate, determination is that of Blx,<sup>4</sup> who found 150.8° C. at 751 mm. pressure. Solid silicon tetrabromide is a pearly crystalline mass which according to Blx melts at 5° C., but according to other observers between -12° C. and -15° C. The solid is heavier than the liquid.

The heats of formation are as follow



Water reacts vigorously with silicon tetrabromide, hydrolysing it with the formation of silicic and hydrobromic acids; litharge produces some lead bromide and lead silicate; ammonia forms the white amorphous, additive compound  $\text{SiBr}_4 \cdot 7\text{NH}_3$ , which is decomposed by water; phosphine,<sup>5</sup> organic bases,<sup>7</sup> and thio- and alkylated ureas also form additive compounds with silicon tetrabromide.<sup>8</sup>

**Silicon Tetra-iodide** (*Tetra-iodosilicane*),  $\text{SiI}_4$ . Silicon tetra-iodide is obtained by the direct combination of its elements, by leading a stream of iodine vapour by means of carbon dioxide, over red-hot silicon,<sup>9</sup> which may be either pure or in the crude form (Gattermann<sup>10</sup>). It has also been prepared by passing iodine vapour heated to 180° C. over silicon heated in a vacuum to 500° C.<sup>11</sup> The vapour of silicon tetra-iodide condenses to the solid state when cooled to atmospheric temperature, and the compound may be crystallised from carbon disulphide, in 1 part of which 2 parts dissolve at 27° C. Silicon tetra-iodide crystallises in regular octahedra, isomorphous with carbon tetra-iodide; it melts at 120.5° C. and boils at 200° C., and its vapour density has been estimated to be 19.12, whilst theory requires 18.56. It burns in the air with a red flame evolving iodine vapour, and is hydrolysed normally by water, whilst with alcohol its reaction is unusual, since it gives no ethyl silicate, but silicic acid, ethyl iodide and hydriodic acid.

<sup>1</sup> Reynolds, *Trans. Chem. Soc.*, 1887, 51, 590.

<sup>2</sup> Gattermann, *Ber.*, 1889, 22, 189.

<sup>3</sup> Gastayson, *Ann. Chim. Phys.*, 1874, [v], 2, 200.

<sup>4</sup> Blx, *Ber.*, 1903, 36, 1218.

<sup>5</sup> Berthelot, *Ann. Chim. Phys.*, 1878, [v], 15, 213.

<sup>6</sup> Besson, *Compt. rend.*, 1890, 110, 210.

<sup>7</sup> Reynolds, *Trans. Chem. Soc.*, 1903, 95, 512.

<sup>8</sup> Reynolds, *Trans. Chem. Soc.*, 1887, 51, 212.

<sup>9</sup> Friedel, *Compt. rend.*, 1868, 67, 98. Friedel and Ladenburg, *Ber.*, 1880, 13, 925.

<sup>10</sup> Gattermann, *Ber.*, 1889, 22, 190.

<sup>11</sup> Guichard, *Compt. rend.*, 1907, 145, 801.

**Mixed Halides of Silicon.**—The existence of a complete series of mixed halides, each containing two different kinds of halogen atom (excepting fluorine), constitutes a peculiar characteristic of the element silicon. These compounds fall naturally into three categories: those containing (1) chlorine and bromine, (2) chlorine and iodine, (3) bromine and iodine.

(1) **Silicon Chlorobromides or Bromochlorosilicanes.**—The three compounds in this category,  $\text{SiCl}_3\text{Br}$ ,  $\text{SiCl}_2\text{Br}_2$ ,  $\text{SiClBr}_3$ , are formed together when hydrogen bromide gas reacts with silicon tetrachloride or silicochloroform at a red heat, or when a mixture of silicon tetrachloride, hydrogen, and bromine is submitted to the influence of the silent electric discharge. When the mixed product is cooled to  $-60^\circ\text{C}$ , silicon chlorotribromide,  $\text{SiClBr}_3$ , appears as a solid, and the other two compounds are separated by fractional distillation of the liquid portion.<sup>1</sup>

Silicon trichlorobromide,  $\text{SiCl}_3\text{Br}$ , also results from the action of bromine on silicochloroform at  $100^\circ\text{C}$ , and on silicon trichlorohydrosulphide,  $\text{SiCl}_3\text{SH}$ , at atmospheric temperature.<sup>2</sup> Two molecules of the dichlorodibromide,  $\text{SiCl}_2\text{Br}_2$ , are changed into  $(\text{SiCl}_3\text{Br} + \text{SiClBr}_3)$  by the silent electric discharge in presence of hydrogen (Besson and Fournier).

*Silicon Trichlorobromide*,  $\text{SiCl}_3\text{Br}$ , is a colourless, fuming liquid which boils at  $80^\circ\text{C}$ , and forms with ammonia the solid compound  $2\text{SiCl}_3\text{Br} \cdot 11\text{NH}_3$ .

*Silicon Dichlorodibromide*,  $\text{SiCl}_2\text{Br}_2$ , is also a colourless, fuming liquid which boils at  $100^\circ\text{C}$  (Friedel) or  $103-105^\circ\text{C}$  (Besson). It forms with ammonia the solid compound  $\text{SiCl}_2\text{Br}_2 \cdot 5\text{NH}_3$ .

*Silicon Chlorotribromide*,  $\text{SiClBr}_3$ , resembles the other two compounds, but boils at  $126-128^\circ\text{C}$  (Besson) or  $140-141^\circ\text{C}$  (Reynolds<sup>3</sup>) and solidifies at  $-39^\circ\text{C}$ . The density of the liquid is 2.132 and its vapour density 10.43 (theory = 10.47). Its compound with ammonia is  $\text{SiClBr}_3 \cdot 11\text{NH}_3$ .

These mixed halides are decomposed by water similarly to the simple halides.

(2) **Silicon Chloro-iodides or Iodochlorosilicanes.**—The chloro-iodides of silicon<sup>4</sup> are prepared by the interaction of silicon tetrachloride and hydrogen iodide in a red-hot tube, or by the action of iodine monochloride on red-hot silicon. Silicon trichloro-iodide,  $\text{SiCl}_3\text{I}$ , also results from heating iodine with silicochloroform in a sealed tube to  $200-250^\circ\text{C}$ . These compounds, which are separated by fractional distillation, resemble the chlorobromides and are similarly decomposed by water; they become coloured on exposure to air owing to the liberation of iodine.

*Silicon Trichloro-iodide*,  $\text{SiCl}_3\text{I}$ , boils at  $113-114^\circ\text{C}$ , and forms with ammonia  $2\text{SiCl}_3\text{I} \cdot 11\text{NH}_3$ .

*Silicon Dichlorodi-iodide*,  $\text{SiCl}_2\text{I}_2$ , boils at  $172^\circ\text{C}$ , and forms  $\text{SiCl}_2\text{I}_2 \cdot 5\text{NH}_3$ .

*Silicon Chlorotri-iodide*,  $\text{SiClI}_3$ , melts at  $2^\circ\text{C}$ , and boils at  $234-237^\circ\text{C}$ ; the composition of its ammonia compound is unknown.

<sup>1</sup> Besson, *Compt. rend.*, 1891, 112, 788, Besson and Fournier, *Compt. rend.*, 1911, 152, 603.

<sup>2</sup> Friedel, *Annal.*, 1867, 143, 118, 1868, 145, 185.

<sup>3</sup> Reynolds, *Trans. Chem. Soc.*, 1887, 51, 590.

<sup>4</sup> Besson, *Compt. rend.*, 1891, 112, 611, 1314.

(3) **Silicon Bromo-iodides or Iodobromosilicanes.**—These compounds resemble the chloro-iodides in manner of preparation and properties.<sup>1</sup> Thus they result from the interaction of silicon tetrabromide and hydrogen iodide at high temperature, and from the action of iodine monobromide on silicon, whilst silicon tribromo iodide can be obtained from iodine and silicon bromide. They are decomposed by water, and oxidised by air with liberation of iodine, whilst with ammonia they form unstable compounds of unknown composition.

*Silicon Tribromo-iodide*,  $\text{SiBr}_3\text{I}$ , is a liquid which may be under-cooled to  $-20^\circ\text{C}$  without solidifying, though its normal melting-point is  $+14^\circ\text{C}$  (Besson), and its boiling-point  $192^\circ\text{C}$ .

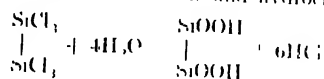
*Silicon Dibromo-iodide*,  $\text{SiBr}_2\text{I}_2$ , melts at  $38^\circ\text{C}$ , and boils at  $230^\circ\text{--}231^\circ\text{C}$ .

*Silicon Bromo-iodide*,  $\text{SiBrI}_2$ , melts at  $53^\circ\text{C}$  and boils at  $255^\circ\text{C}$ .

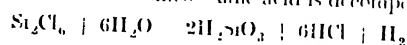
**Halogen Derivatives of Silico-ethane.**  $\text{Si}_2\text{H}_6$ , *Hexachlorosilico-ethane*,  $\text{Si}_2\text{Cl}_6$ .—This compound is formed by the action of chlorine upon the corresponding iodide,  $\text{Si}_2\text{I}_6$ , or by gently heating this compound with mercuric chloride;<sup>2</sup> much heat is evolved and hexachlorosilico-ethane,  $\text{Si}_2\text{Cl}_6$ , distils. Troost and Hautefeuille<sup>3</sup> obtained this compound by the union of silicon and its tetrachloride, by passing the vapour of the latter over white-hot silicon; and Gattermann and Weinig<sup>4</sup> found that it was formed, together with silicon tetrachloride, when chlorine acted on crude silicon, and separated the two compounds by fractional distillation.

Hexachlorosilico-ethane is a colourless, fuming liquid which solidifies at  $-1^\circ\text{C}$ , and boils at  $116\text{--}118^\circ\text{C}$ . Its density at  $0^\circ\text{C}$ , is 1.58, and its vapour density at  $239^\circ\text{C}$  is 9.7 (theory requires 9.92).

Above  $350^\circ\text{C}$ , the vapour of hexachlorosilico-ethane begins to dissociate into silicon tetrachloride and silicon, and this dissociation continues up to  $1000^\circ\text{C}$ , above which temperature the vapour becomes stable again. Consequently, when silicon tetrachloride vapour is passed over silicon heated above  $1000^\circ\text{C}$  in a porcelain tube hexachlorosilico-ethane is formed, and is decomposed again in a cooler part of the tube; by this means silicon is transported along the tube from the hotter to the cooler part (Troost and Hautefeuille). Hexachlorosilico-ethane reacts with water to form silico-oxalic and hydrochloric acids, thus:



Solutions of ammonia and potash produce silicic acid or a silicate with evolution of hydrogen. Since silico-oxalic acid is decomposed by alkalis:



With gaseous ammonia there is formed the solid compound  $\text{Si}_2\text{Cl}_6 \cdot 10\text{NH}_3$ , which begins to lose ammonia at  $100^\circ\text{C}$ , and is slowly decomposed by water.

Phosphine does not unite with hexachlorosilico-ethane, but is reduced by it, even at  $-10^\circ\text{C}$  to the solid hydrogen phosphide,

<sup>1</sup> Friedel, *Ber.*, 1869, 2, 60.

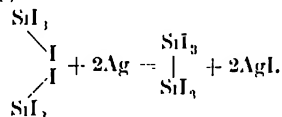
<sup>2</sup> Friedel, *Compt. rend.*, 1871, 73, 1011.

<sup>3</sup> Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [v], 7, 461.

<sup>4</sup> Gattermann and Weinig, *Ber.*, 1891, 27, 1943.

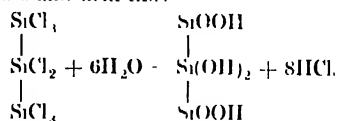
**Hexabromosilico-ethane,  $\text{Si}_2\text{Br}_6$ .**—This compound<sup>1</sup> is formed by the action of bromine on a carbon disulphide solution of the corresponding iodide, the liberated iodine being removed by shaking with mercury. It is also among the products of the action of the silent electric discharge on silicobromoform,  $\text{SiHBr}_3$ .<sup>2</sup> It forms tabular crystals, which melt at  $95^\circ \text{C}$ . and boil at  $265^\circ \text{C}$ . Hexabromosilico-ethane resembles the corresponding chlorine compound in its behaviour towards water and alkalis.

**Hexa-iodosilico-ethane,  $\text{Si}_2\text{I}_6$ .**—The manner of preparation of hexa-iodosilico-ethane is of interest because this compound is the source of hexachlorosilico-ethane and hexabromosilico-ethane, and in its formation the linkage of silicon atoms takes place. The process is one of condensation, to which numerous analogies are furnished in organic chemistry. Thus Friedel and Ladenburg<sup>3</sup> obtained hexa-iodosilico-ethane by heating the tetra-iodide with finely divided silver at  $290 - 300^\circ \text{C}$ . for some hours :



Unchanged tetra-iodide was then removed from the product by washing it with carbon disulphide, in which the tetra-iodide is much more soluble than hexa-iodosilico-ethane, and the latter was then crystallised from hot carbon disulphide. Hexa-iodosilico-ethane forms colourless, hexagonal, doubly refractive plates, which melt *in vacuo* at  $250^\circ \text{C}$ . with partial decomposition, silicon tetra-iodide and a lower iodide supposed to be silicon di-iodide,  $\text{SiI}_2$ , being produced. Hexa-iodosilico-ethane fumes in the air, and resembles the corresponding chlorine and bromine compounds in its behaviour towards water and alkalis.

**Halogen Derivatives of Silicopropane,  $\text{Si}_3\text{X}_8$ .** *Octachlorosilicopropane,  $\text{Si}_3\text{Cl}_8$ ,* is among the products of the action of chlorine on crude silicon, of which it forms about 0.5 to 1 per cent ; it is separated from the tetrachloride and hexachlorosilico-ethane formed with it by fractional distillation.<sup>4</sup> Its formation, moreover, appears to depend on the presence of magnesium silicide in the crude silicon.<sup>5</sup> Octachlorosilicopropane is a colourless liquid boiling at  $215 - 218^\circ \text{C}$ .<sup>6</sup> ; after solidification it melts at  $-67^\circ \text{C}$ . ; it is decomposed by cold water, forming mesosilico-oxalic acid thus



*Octabromosilicopropane,  $\text{Si}_3\text{Br}_8$ ,* is formed among other products<sup>7</sup> of the action of the silent electric discharge on silicobromoform,  $\text{SiHBr}_3$ . It is a solid melting at  $133^\circ \text{C}$ .

<sup>1</sup> Friedel and Ladenburg, *Annalen*, 1880, 203, 253.

<sup>2</sup> Besson and Fournier, *Compt. rend.*, 1910, 151, 1055.

<sup>3</sup> Friedel and Ladenburg, *Annalen*, 1880, 203, 247.

<sup>4</sup> Gattermann and Wenig, *Ber.*, 1894, 27, 1943.

<sup>5</sup> Gattermann and Ellery, *Ber.*, 1899, 32, 1114.

<sup>6</sup> Besson and Fournier, *Compt. rend.*, 1909, 148, 839.

<sup>7</sup> Besson and Fournier, *Compt. rend.*, 1910, 151, 1055.

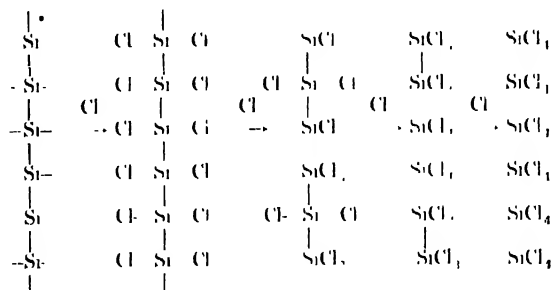
**Halogen Derivatives of Silicobutane,  $\text{Si}_4\text{X}_{10}$ .**—The chlorine and bromine derivatives are known.

**Decachlorosilicobutane,  $\text{Si}_4\text{Cl}_{10}$ .**<sup>1</sup> is among the products of the action of the electric discharge on a mixture of hydrogen and silicon tetrachloride. It is a liquid boiling at  $119-151^\circ\text{C}$ . under 15 mm. pressure.

**Decabromosilicobutane  $\text{Si}_4\text{Br}_{10}$** <sup>2</sup> is formed, together with its homologues, when the silent electric discharge acts on silicobromoflorm. It is a crystalline solid, melting with decomposition at  $185^\circ\text{C}$ .

**Halogen Derivatives of Silicopentane and Silicohexane.** The chlorinated derivatives  $\text{Si}_5\text{Cl}_{12}$  and  $\text{Si}_6\text{Cl}_{14}$  have been isolated by Besson and Fournier<sup>3</sup> from among the products of the action of the silent electric discharge on a mixture of hydrogen and silicon tetrachloride.  $\text{Si}_5\text{Cl}_{12}$  is an extremely viscous liquid boiling at  $190^\circ\text{C}$ . 15 mm.  $\text{Si}_6\text{Cl}_{14}$  is a white solid which melts with decomposition at  $170^\circ\text{C}$  and sublimes in a vacuum at  $200^\circ\text{C}$ .

The conditions of formation of the higher chlorides of silicon have recently been investigated by Martin<sup>4</sup> who has prepared hexachlorosilico-ethane and octachlorosilico-propane in quantity, as well as smaller amounts of the higher chlorides, together with silicon tetrachloride, by the action of chlorine on 50 per cent. ferro-silicon at temperatures not exceeding  $310^\circ\text{C}$ . Martin affirms that the higher chlorides are first formed by the chlorination of chains of silicon atoms, which probably exist in ferro-silicon as well as in the free solid element, and that these chains, by further chlorination, yield simpler products, and finally silicon tetrachloride, according to the scheme



The alternative view, of Gattermann and Weinlig,<sup>5</sup> that silicon tetrachloride is first formed and then combines with silicon to form higher chlorides, is controverted on the ground that the production of hexachlorosilico-ethane from silicon tetrachloride and silicon is an endothermic reaction unlikely to take place at so low a temperature as  $300^\circ\text{C}$ ., that the yield of hexachlorosilico-ethane reaches its maximum at a still lower temperature, viz.  $180-200^\circ\text{C}$ . and that when silicon tetrachloride is distilled over silicon or ferro-silicon between  $200^\circ\text{C}$ . and  $340^\circ\text{C}$ . the formation of hexachlorosilico-ethane is not

<sup>1</sup> Besson and Fournier, *Compt. rend.*, 1909, 145, 839, 149, 34.

<sup>2</sup> Besson and Fournier, *Compt. rend.*, 1910, 151, 105.

<sup>3</sup> Besson and Fournier, *ibid.*

<sup>4</sup> Martin, *Trans. Chem. Soc.*, 1911, 105, 2836.

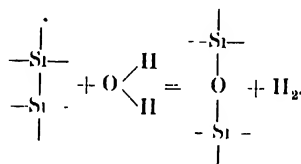
<sup>5</sup> Gattermann and Weinlig, *Ber.*, 1891, 27, 1943.



observed, but that, on the other hand, hexachlorosilico-ethane unites with chlorine at 300° C., producing silicon tetrachloride. From hexachlorosilico-ethane Martin<sup>1</sup> has prepared the following ethoxy-derivatives:

Substance	Boiling point under 34 mm	Density	Refractive Index D line
Si <sub>2</sub> Cl <sub>6</sub>	60.5° C.	1.5624 at 15° C.	1.4718 at 18° C.
Si <sub>2</sub> Cl <sub>5</sub> (OEt)	84° C.	1.388 .. 20° C.	1.4568 .. 11.5° C.
Si <sub>2</sub> Cl <sub>4</sub> (OEt) <sub>2</sub>	101° C.	1.270 .. 20° C.	1.4432 .. 11.5° C.
Si <sub>2</sub> Cl <sub>3</sub> (OEt) <sub>3</sub>	122° C.	1.163 .. 20° C.	1.4333 .. 11.5° C.
Si <sub>2</sub> Cl <sub>2</sub> (OEt) <sub>4</sub>	—	—	—
Si <sub>2</sub> Cl(OEt) <sub>5</sub>	138° C.	1.092 .. 17° C.	1.4205 .. 11.5° C.
Si <sub>2</sub> (OEt) <sub>6</sub>	141° C.	0.9718 .. 17° C.	1.4134 .. 11.5° C.

These compounds react with alkalis with the evolution of hydrogen and the interpolation of an oxygen atom between two silicon atoms, thus:



### SILICON OXYCHLORIDES

Of the oxyhalides of silicon which might be expected to exist, several oxychlorides alone have been obtained, and of these the simplest, SiOCl<sub>2</sub>, is unknown. Our knowledge of silicon oxychlorides is due to the researches of Friedel and Ladenburg,<sup>3</sup> and of Troost and Hautefeuille,<sup>4</sup> and the subject appears scarcely to have been investigated since 1881.

The following oxychlorides have been prepared, the molecular formulae of several of them having been established by vapour-density determinations:

	Boiling-point °C	Vapour Density (Air = 1)
Si <sub>2</sub> OCl <sub>6</sub>	137-138	10.05 (theory = 9.86)
Si <sub>4</sub> O <sub>3</sub> Cl <sub>10</sub>	152-154	9
Si <sub>4</sub> O <sub>4</sub> Cl <sub>8</sub>	198-202	15.5 (theory = 15.9)
Si <sub>8</sub> O <sub>10</sub> Cl <sub>12</sub>	c. 300	31.2 (theory = 28.0)
(Si <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> ) <sub>n</sub>	above 400	—
(Si <sub>4</sub> O <sub>7</sub> Cl <sub>2</sub> ) <sub>n</sub>	440	—

The oxychloride Si<sub>2</sub>OCl<sub>6</sub> is formed when a mixture of chlorine and oxygen is passed over crystallised silicon heated to 800° C., when

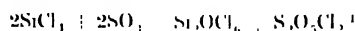
<sup>1</sup> Martin, *Trans. Chem. Soc.*, 1914, 105, 2860

<sup>2</sup> Martin, *Ber.*, 1912, 45, 2097; 1913, 46, 2442, 3289

<sup>3</sup> Friedel and Ladenburg, *Annalen*, 1868, 147, 361; *Bull. Soc. chim.*, 1871, [n], 16, 244.

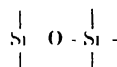
<sup>4</sup> Troost and Hautefeuille, *Annalen*, 1871, 163, 146, 371; *Ann. Chim. Phys.*, 1876 [v], 7, 453; *Bull. Soc. chim.*, 1881, [n], 35, 360.

the vapour of silicon tetrachloride is passed over felspar heated to whiteness in a porcelain tube, and by the interaction of silicon tetrachloride and sulphur trioxide at 50° C.



It is a colourless liquid which fumes in the air and reacts with water, forming hydrochloric and silicic acids, whilst with alcohol and also with zinc ethyl, it yields the ester  $\text{Si}_2\text{O}(\text{OC}_2\text{H}_5)_6$ . The higher oxychlorides were obtained by passing this oxychloride over heated felspar, or by leading a mixture of it and oxygen through a red-hot porcelain tube, the product being then submitted to fractional distillation.

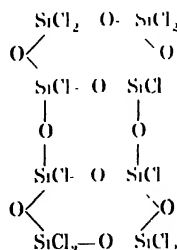
All of these oxychlorides consist of polymerised  $\text{SiO}_2$  molecules, some of whose oxygen atoms have been replaced by atoms of chlorine. Moreover, they contain chains or rings of alternative silicon and oxygen atoms thus:



which are so characteristic of the element silicon especially in the natural silicates. Although there is no evidence as to the actual constitution of these compounds, it is reasonable to suppose that  $\text{Si}_4\text{O}_4\text{Cl}_8$  possesses a cyclic constitution, to which it is interesting to note, a phenyl derivative prepared by Kipping<sup>2</sup> from  $\text{SiCl}_4$  corresponds:



$\text{Si}_4\text{O}_4\text{Cl}_8$ , however, is most easily represented as a chain compound:  $\text{Cl}_3\text{Si} \cdot \text{O} \cdot \text{SiCl}_2 \cdot \text{O} \cdot \text{SiCl}_2 \cdot \text{O} \cdot \text{SiCl}_3$  while  $\text{Si}_8\text{O}_{10}\text{Cl}_{12}$  may possibly consist of two eight-membered rings linked through oxygen, thus:



Whether these constitutional formulae adequately represent the facts or not, it is plain that the existence of these complex oxychlorides is connected with that of the similarly complex silicic acids of which the natural silicates are salts.

<sup>1</sup> Sanger and Riegel, *Zeitsch. anorg. Chem.*, 1913, **80**, 252.

<sup>2</sup> Kipping, *Trans. Chem. Soc.*, 1912, **101**, 2125.

the prismatic faces are entirely absent; generally the pyramidal faces are unequally developed, three alternate faces being large, and often almost crowding out the other three. The three alternate pyramidal faces are the faces of a rhombohedron, which is a hemihedral form derived from the hexagonal pyramid; and a quartz crystal really consists of two such hemihedral forms combined. It is therefore said to belong to the rhombohedral division of the hexagonal system. Another feature of quartz crystals is the horizontal striae on their prism faces, and a further one the frequent presence of other small faces which lie between the pyramid and prism faces on alternate corners of the crystal. These small faces cause the crystals to appear asymmetric, *i.e.* to be without a plane of symmetry; and there are two kinds of such asymmetric crystals, which are related to one another as object and image, or as right and left hand. The crystals are therefore said to be enantiomorphous, and are conveniently called right- and left-handed crystals (see Fig. 5).

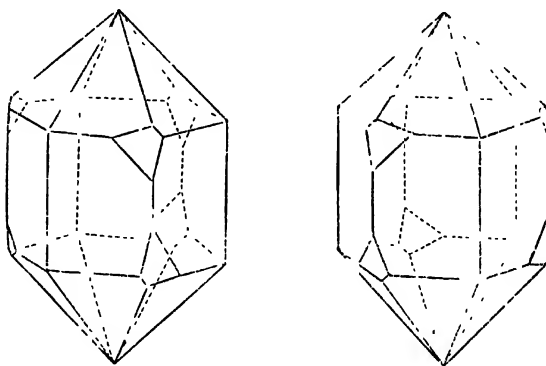


Fig. 5 - Enantiomorphous quartz crystals

Now enantiomorphous crystals are known amongst organic compounds, and are there associated with optical activity of the compounds, as, for instance, in the case of the tartaric acids. Quartz, too, is optically active, *i.e.* it rotates the plane of polarisation of a beam of polarised light that passes through it in the direction of the principal axis; and the opposite crystals are opposite in their optical activity. In the case of organic compounds optical activity is a molecular property which persists when the compound is in the state of fusion or solution; it arises from the presence within each molecule of one or more "asymmetric" carbon atoms. In the case of quartz, however, optical activity is a property of the crystal rather than of the molecule of silica; it depends upon the way in which these molecules are built up within the crystal.

A section of quartz, 1 mm. thick, cut perpendicular to the principal axis of the crystal, rotates the plane of yellow (D) light through  $22^\circ$  and of blue (G) light through  $43^\circ$ .

Such a section shows interference colours in the polariscope.

The refractive index of quartz for sodium (D) light  $\mu_D = 1.541147^1$ , its density at 0° C. is 2.6507, and falls to 2.6109 at 100° C., its hardness on Moh's scale is 7, its specific heat from 0° to 100° C. is given by the formula

$$\gamma_t = 0.1737 + 0.000394t - 0.0027t^2$$

between 100° C. and 1200° C. it becomes constant = 0.5.

Quartz melts in the oxyhydrogen flame (1600–1750° C.), producing a glass whose density at atmospheric temperature is 2.20; it begins to vaporise between 1700° C. and 1750° C. Before reaching its melting-point, however, it undergoes modification. Above 575° C. ordinary quartz, which may be called  $\alpha$ -quartz, undergoes a reversible change<sup>2</sup> into  $\beta$ -quartz, which differs from the former in optical properties and in the kind of etching produced upon it by hydrofluoric acid; whilst above 800° C. quartz is converted into tridymite<sup>3</sup>. These facts throw some light on the temperature conditions of formation of quartz and tridymite.

*Artificial Production of Quartz* Many experiments have been made upon the production of quartz in the presence of water, and in the dry way. Christ-scholt,<sup>4</sup> basing his experiments on previous work of Schafhäutl and Senarmont, obtained quartz by heating an aqueous solution of colloidal silica to 250° C. for some months. Also he added hydrofluoboric acid to the silica solution and obtained crystals of cristobalite at 180° C. to 228° C., quartz at 240°–300° C., and tridymite at 310°–360° C. Quartz has also been obtained by heating gelatinous silica with caustic potash and alumina, and with ammonium fluoride. Allen produced fine crystals of quartz by heating a mixture of magnesium ammonium chloride, sodium metasilicate and water at 100°–150° C. for three days in a steel bomb.<sup>5</sup>

Methods for the production of quartz in the dry way include the heating of amorphous silica with sodium or lithium tungstate to 750°<sup>6</sup> and of quartz glass to 700°–750° C. in the vapours of alkali chlorides<sup>7</sup>; but in most of the attempts to obtain quartz in the dry way tridymite was formed because the temperature attained was above 800° C., the transition temperature of quartz into tridymite.

*Uses of Quartz* Quartz has been valued from the earliest times on account of its transparency and hardness. It is employed in the form of gems and ornaments, for making spectacle-glasses (from "pebbles"), lenses and prisms, and unalterable chemical weights, whilst the commoner kinds are used for cutting and polishing purposes and in the manufacture of porcelain and glass. Agate is employed for making mortars and pestles for grinding hard solids, and for the bearings of chemical balances.

A recently developed and important use of quartz is for the manufacture of quartz glass.<sup>8</sup> Transparent quartz of good quality is fused in an electric furnace, and the liquid worked like glass into various

<sup>1</sup> Rubens, *Wied. Annalen*, 1895, 54, 476.

<sup>2</sup> Wright and Larsen, *Amer. J. Sci.*, 1909, [iv], 28, 293.

<sup>3</sup> Day and Shepherd, *Amer. J. Sci.*, 1906, [iv], 22, 276. Stein, *Zeitsch. anorg. Chem.*, 1907, 55, 159.

<sup>4</sup> Christ-scholt, *Compt. rend.*, 1887, 104, 602.

<sup>5</sup> Cited by Day and Shepherd, *loc. cit.*

<sup>6</sup> Hautefeuille, *Bull. Soc. min.*, 1878, 1, 1.

<sup>7</sup> Brun, *Arch. Sci. phys. nat.*, 1908, [iv], 25, 610.

<sup>8</sup> Vide Bottomley, *J. Soc. Chem. Ind.*, 1917, 36, 577.

forms of chemical apparatus or drawn out into threads of extraordinary delicacy, which on account of their strength are employed for suspensions in galvanometers and other instruments (Boys). Quartz glass has several advantages over glass containing basic oxides. Its coefficient of linear expansion is only 0.000000449; or, according to Harlow,<sup>1</sup> the cubical coefficient of expansion of fused silica is  $99.8 \times 10^{-8}$  for the temperature interval 0°–100° C., and  $144.7 \times 10^{-8}$  for the interval 0°–181° C. In consequence of this very small coefficient of expansion, quartz glass can be heated to a red heat and plunged into water without fracture; it may therefore be employed in the distillation of valuable liquids and of sulphuric acid, as well as for thermometry; whilst the fact that it contains no alkali to be extracted by water makes it of service in chemical analysis. The density of quartz glass is 2.21, its hardness 5; its refractive index for the D line,  $\mu_D = 1.45818$ .<sup>2</sup>

A non-transparent kind of silica glass, known as "vitreosil," is prepared by passing a powerful electric current through a carbon rod or plate embedded in sand. The sand fuses round the carbon, and when the latter is removed an object of translucent silica remains, which may be glazed externally by subsequent fusion or worked on a lathe. Vitreosil is employed for making crucibles, dishes, combustion tubes, plates, and other articles.

**Tridymite.**—Tridymite (*τρίδυμος*, threefold) is a second crystalline form of silica, discovered by G. von Rath,<sup>3</sup> which occurs in trachyte and other volcanic rocks. It forms hexagonal plates which are combinations of prisms and pyramids and probably orthorhombic; frequently it is found in twillings or triplets, whence its name is derived. That tridymite has been formed at high temperature is shown by its artificial production under these conditions. Indeed G. Rose observed the conversion of quartz into tridymite by simple ignition, and Brinn found that quartz glass is converted into tridymite when heated between 800° C. and 1000° C. in the vapours of alkali chlorides. Tridymite can be conveniently prepared<sup>4</sup> by fusing sodium silicate with three times its weight of sodium phosphate for six hours at 1000° C. extracting with water and washing. The residue consists of microscopic hexagonal tablets of density 2.310. As stated under quartz, 800° C. is the transition temperature, below which quartz is stable, above which tridymite. Quartz and tridymite are both polymorphic forms of  $\text{SiO}_2$ , but tridymite has probably the simpler molecule of the two, and so is more stable at high temperatures.

The density of tridymite is 2.30,<sup>5</sup> its hardness 7, its refractive index<sup>6</sup>  $\mu_D = 1.476$ , its melting-point about 1625° C.

**Cristobalite**, another crystalline modification of silica described as pseudo-cubic, may be obtained by heating powdered transparent silica glass in a porcelain furnace. It has a density of 2.319, and is distinguished from tridymite by becoming isotropic when heated for a short time at 250° C.<sup>4</sup>

**Amorphous Silica.**—Amorphous silica occurs naturally as opal and hyalite. Opal is colourless or variously coloured, has a vitreous fracture,

<sup>1</sup> Harlow, *Proc. Physical Soc.*, 1911, 24, 30.

<sup>2</sup> Gifford and Shenstone, *Proc. Roy. Soc.*, 1904, 73, 201.

<sup>3</sup> Von Rath, *Pogg. Annalen*, 1868, 133, 507, 135, 437.

<sup>4</sup> Schwartz, *Zeitsch. anorg. Chem.*, 1912, 76, 422.

<sup>5</sup> Rammelsberg, *Ber.*, 1872, 5, 1006.

<sup>6</sup> Mallard, *Bull. Soc. min.*, 1890, 13, 161.

a density of 2.2, and contains a proportion of water which ranges between 2 and 13 per cent. There is no doubt that opal is of a colloidal nature, and has been formed by the drying up of gelatinous silica; for an amorphous mass, practically identical with opal, can be produced from the colloidal silica acid separated from an alkali-silica solution by strong acid.<sup>1</sup> Moreover, the siliceous sinter deposited in the neighbourhood of hot siliceous springs is a kind of opal, and at Plombières, in France, opal has been formed by the action of water on Roman cement.<sup>2</sup> Precious, iridescent opal has been formed in the cavities of igneous rocks by the action of hot water.

Artificial amorphous silica is prepared by decomposing silicon tetrachloride with water or an alkali silicate with acid. When, for example, concentrated hydrochloric acid is added to a solution of soluble glass, which is sodium metasilicate,  $\text{Na}_2\text{SiO}_3$  "gelatinous silica" or metasilicic acid separates. The mass is carefully evaporated and ignited, and the silica is thereby rendered insoluble by a process of polymerisation which accompanies dehydration. The residue is then digested with dilute hydrochloric acid to dissolve oxide of iron or other impurity, as well as sodium chloride, and finally washed with water, dried, and ignited.

Thus obtained, amorphous silica is a white, mobile powder of density 2.22 and melting-point  $1750-1780^\circ\text{C}$ . When it is strongly heated for some time the density gradually rises owing to the formation of tridymite.

**Chemical Properties of Silica.** The different forms of silica differ in chemical reactivity. This is shown by heating each variety, finely powdered, with 1 per cent. hydrofluoric acid for an hour. Under these conditions 5.2 per cent. of the quartz dissolves, 20.3 per cent. of the tridymite, 25.8 per cent. of the cristobalite and 52.9 per cent. of the amorphous silica.<sup>3</sup> All kinds, however, are insoluble in water and all acids except hydrofluoric acid, which forms silicon tetrafluoride according to the reaction:



If pure silica is mixed with excess of aqueous hydrofluoric acid in a platinum dish and the liquid is evaporated, the tetrafluoride passes away with the steam. Since, however, water hydrolyses silicon tetrafluoride, it is necessary to add a little concentrated sulphuric acid to prevent this action, and then the whole may be vapourised without residue. Quartz crystals are slowly etched by hydrofluoric acid, their different faces showing different characteristic markings. Dried gelatinous silica reacts with molten metaphosphoric acid to form a silicophosphoric oxide,<sup>4</sup> but silica does not displace phosphoric oxide from a metaphosphate; hence particles of this substance float in a bead of fused microcosmic salt. Amorphous silica dissolves in solutions of caustic alkalis, which, however, scarcely act on quartz. Silica displaces carbon dioxide from sodium carbonate when it is fused with this salt, thereby forming a soluble glass. A convenient test for silica consists in introducing it into a sodium carbonate bead on a loop

<sup>1</sup> L. Bourgeois, *Reproduction artificielle des miréaux*, 1881, p. 93.

<sup>2</sup> A. Daubrée, *Études synthétiques de géologie expérimentale*, 1879, p. 189.

<sup>3</sup> Schwarz, *Zeitsch. anorg. Chem.*, 1912, 76, 122.

<sup>4</sup> Hautefeuille and Margottet, *Compt. rend.*, 1883, 96, 1052; 1884, 99, 789.

of platinum wire. When sodium carbonate is fused alone it crystallises, and becomes opaque on cooling; when silica is fused with it the bead on cooling appears as a transparent glass. Hydrated amorphous silica dissolves in alkali carbonate solutions; this fact accounts for the appearance of this substance in spring waters, and furnishes the means by which silica circulates in nature.

Silica is reduced when heated with potassium, calcium or magnesium, forming silicon and a metallic silicide and sometimes silicate; it appears, moreover, that silicon monoxide is produced when silica is heated electrically in an inert atmosphere with sufficient carbon or carbonadium to remove half its oxygen.<sup>1</sup> When silica is mixed with carbon and heated in hydrogen sulphide, silicon disulphide (*q.v.*) is formed.

The reduction of silica by hydrogen at 1350°-1400° C. has been studied by von Wartenberg.<sup>2</sup>

**Hydrates of Silica: the Silicic Acids.**—It has already been seen that hydrated silica exists naturally as opal, and is formed artificially by decomposing silicon tetrachloride with water, or soluble glass with hydrochloric acid.

Theoretically two varieties of monosilicic acid are derivable from  $\text{SiO}_2$ : orthosilicic acid,  $\text{Si}(\text{OH})_4$ , and metasilicic acid,  $\text{SiO}(\text{OH})_3$ . That these simple formulae represent actual chemical compounds, however, cannot be affirmed, though products closely corresponding to them in composition may be obtained by suitable means.

Thus, if the gelatinous product of the action of water on silicon tetrachloride is washed with benzene and dry ether and then quickly dried at atmospheric temperature, the amorphous white powder obtained corresponds closely to the composition of orthosilicic acid,  $\text{H}_4\text{SiO}_4$ , but it rapidly loses water when left in the air.<sup>3</sup>

A product corresponding approximately to the formula  $\text{H}_2\text{SiO}_3$ , and which is therefore called metasilicic acid, is obtained in the following way.

A dilute solution of soluble glass or sodium metasilicate,  $\text{Na}_2\text{SiO}_3$ , is acidified with dilute hydrochloric acid. No precipitate is formed, but a form of silicic acid is present in the clear liquid. This liquid is then submitted to dialysis. It is placed in a dialyser—that is, a flat drum with a bottom consisting of parchment paper—which is floated on the surface of running water in a large dish. Parchment is a “semi-permeable membrane” through which the small molecules or ions of “crystalloids,” such as hydrochloric acid and sodium chloride, can pass, but which the molecules of “colloids,” of which silicic acid is an example, are too large to penetrate. Thus the sodium chloride and hydrochloric acid are washed away, and pure, dialysed silicic acid remains. Pure aqueous silicic acid may also be conveniently obtained by bringing silicon tetrachloride vapour into water through mercury and dialysing the solution.<sup>4</sup> Such an aqueous colloid is called a “hydrosol” or “sol”; it is not a true solution, but a suspension of ultra-microscopic particles.<sup>5</sup> It, however, possesses a faintly acid reaction, and therefore contains some silicic acid in true solution. According

<sup>1</sup> *D.R.P.*, No. 189833

<sup>2</sup> Von Wartenberg, *Zeitsch. anorg. Chem.*, 1912, 79, 71

<sup>3</sup> Norton and Roth, *J. Amer. Chem. Soc.*, 1897, 19, 832

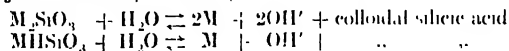
<sup>4</sup> Ebler and Feliner, *Ber.*, 1911, 44, 1915

<sup>5</sup> For a further discussion of the properties of colloids, the large and growing literature of the subject must be consulted

to Ebler<sup>1</sup> the specific conductivity of a solution of silicic acid obtained from 40 grams of silicon tetrachloride and 2000 c.c. of water is  $K_{18}^{\circ} = 1.7 \times 10^{-5}$  after dialysing for twenty-two days. Aqueous silicic acid is colourless and tasteless, and may be concentrated by boiling until it reaches a strength of 14 per cent. It is inclined, however, to gelatinise during evaporation, and when the concentrated liquid stands for a few days the whole is converted into a transparent jelly, the "hydrosol" or "gel." Thus the hydrosol and the hydrogel are two forms of the same product, the former being converted into the latter by catalytic agents. The structure of silicic acid "gel" has been elucidated by Zsigmondy.<sup>2</sup> It serves as a medium in which certain inorganic salts may be crystallised.<sup>3</sup>

If the sol of silicic acid evaporates over sulphuric acid at atmospheric temperature in a vacuum, a transparent glass remains which corresponds very nearly to the formula  $H_2SiO_4$ , and a product of similar composition is obtained by washing precipitated "gelatinous silica" with 90 per cent. alcohol.<sup>4</sup>

Nevertheless it cannot be said that definite compounds corresponding to the formulae  $H_2SiO_4$  and  $H_2SiO_3$  exist. Since silicic acid is colloidal its molecules must be large, and the formulae  $mSiO_2 \cdot 2nH_2O$  and  $mSiO_2 \cdot nH_2O$ , where  $m$  and  $n$  are approximately equal, large whole numbers more nearly represent the facts. Tschermak,<sup>5</sup> who has studied the velocities of dehydration of silicic acids derived from various minerals, has shown that the curves indicating these velocities change abruptly in direction at certain compositions; thus, it is claimed, indicates the existence of definite hydrates of silica. Recent research, however, has thrown doubt on the existence of any definite hydrate of silica.<sup>6</sup> Hydrated silica performs the functions of a very weak acid. Its only soluble salts are those of the alkali metals, and these are hydrolysed in aqueous solution into alkali hydroxides and colloidal silicic acid; this is proved by determination of the freezing-points and electric conductivities of the solutions.<sup>7</sup> Hydrolysis of the silicates  $M_2SiO_3$  and  $MHSiO_3$  according to the schemes



is practically complete at a dilution of 18 litres, whilst silicates of the type  $M_2Si_3O_{11}$  need to be diluted to 128 litres for complete hydrolysis. It may be concluded from this that in natural waters containing alkali silicate in very dilute solution the silicic acid is always present in the free, colloidal state.

Very weak acids form ammonium salts with difficulty, and silicic acid shares with stannic and a few other acids the inability to form an ammonium salt. Hence when an ammonium salt is added to sodium silicate solution gelatinous silicic acid is at once precipitated.

<sup>1</sup> Ebler and Fellner, *Ber.*, 1911, 44, 191.

<sup>2</sup> Zsigmondy, *Zeitsch. anorg. Chem.*, 1911, 71, 355.

<sup>3</sup> Hartschick, *Zeitsch. Chem. Ind. Kolloid.*, 1912, 10, 77.

<sup>4</sup> Butureau, *Ann. Sci. Univ. Jussieu*, 1901, 1, 319.

<sup>5</sup> Tschermak, *Zeitsch. physikal. Chem.*, 1905, 53, 319, *Chem. Centr.*, 1906, ii, 552, *Zeitsch. anorg. Chem.*, 1909, 63, 230, 1910, 66, 199.

<sup>6</sup> Mugge, *Centr. Min.*, 1908, 129, van Bemmelen, *Zeitsch. anorg. Chem.*, 1908, 59, 225; Le Chatelier, *Compt. rend.*, 1908, 147, 660.

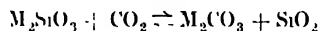
<sup>7</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1893, 12, 773, Kahlenberg and Lincoln, *J. physical Chem.*, 1898, 2, 77.



The heats of reaction of silicic acid with different amounts of sodium hydroxide have been measured by Thomsen.<sup>1</sup> These are very small, as is consistent with the weakness of the acid and its very imperfect reaction with the base. The following is one of the values obtained by Thomsen at 18–20° C., the dilution being with 200 molecules of water:



The equilibrium between carbon dioxide and silica when competing for the same base as in the reaction



has been studied by von Wittorf,<sup>2</sup> who heated alkali carbonates with silica to temperatures ranging between 800° C. and 1300° C. in an atmosphere of carbon dioxide, the pressure of which was regulated between 0.07 and 1.0 atmosphere. It was found that the power possessed by silica to expel carbon dioxide increased with temperature, but that the direction of the reaction depended upon whether the pressure of the superimposed carbon dioxide was increasing or decreasing. The proportion of carbonate present under similar conditions of temperature and pressure increased with rise of atomic weight in the series  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ .

These conclusions are in accord with the principles of chemical dynamics;  $\text{CO}_2$ , considered as a molecule, no doubt has a greater affinity for bases than  $\text{SiO}_2$ , but the great difference in physical properties between these two substances modifies the influence of chemical affinity. Thus, whilst silica displaces carbon dioxide from a carbonate at high temperature, especially if the expelled carbon dioxide is allowed to escape freely, because the latter is volatile whilst the former is not, carbonic acid displaces silicic acid from aqueous solutions of its salts, not only on account of superior affinity, but because of the insolubility of the latter. These considerations have a terrestrial significance. Thus the igneous rocks contain silicates rather than carbonates; for if atmospheric carbon dioxide was present when they were formed, it could not successfully compete with silica at the temperature of their formation. Since, however, the cooling of these rocks and the advent of water on our globe, atmospheric carbon dioxide has been perpetually disintegrating natural silicates, setting free silica, and forming carbonates instead.

#### THE SILICATES

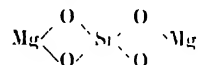
It has been seen that silica is the anhydride of a very feeble acid, silicic acid, which is supposed to exist in the ortho- and meta- forms,  $\text{Si}(\text{OH})_4$  and  $\text{SiO}(\text{OH})_2$  respectively; but that the acids actually obtainable approximate rather than actually conform to these simple types, because the chemical union between silica and water is of such a feeble and complex character as apparently to lack definiteness. The silicates are, however, more definite in composition than the acid itself, though only in the case of a few organic silicates are their molecular weights known. These, however, are of the utmost importance

<sup>1</sup> Thomsen, *Thermochemische Untersuchungen*, 1906, p. 64.

<sup>2</sup> Wittorf, *Zeitsch. anorg. Chem.*, 1904, 39, 187.

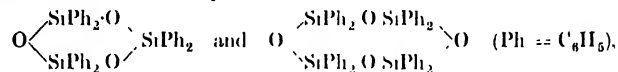
because they alone throw any certain light upon the constitution of silicates in general.

Thus the existence of ethyl orthosilicate, whose molecular formula is  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , to a certain extent justifies the formula



for the mineral olivine whose empirical composition is  $2\text{MgO} \cdot \text{SiO}_2$ , whilst ethyl metasilicate,  $\text{SiO}(\text{OC}_2\text{H}_5)_2$ , represents a type to which belongs a class of natural silicates of which wollastonite,  $\text{CaSiO}_3$ , is an example.

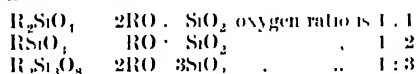
The preparation by Kipping<sup>1</sup> of the organo silicic acids  $\text{SiPh}_2(\text{OH})_2$ ,  $\text{HO} \cdot \text{SiPh}_2 \cdot \text{O} \cdot \text{SiPh}_2 \cdot \text{OH}$  and  $\text{HO} \cdot \text{SiPh}_2 \cdot \text{O} \cdot \text{SiPh}_2 \cdot \text{O} \cdot \text{SiPh}_2 \cdot \text{OH}$ , as well as the cyclic anhydrides,



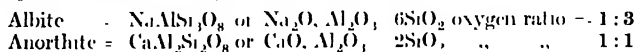
affords valuable information as to the probable structure of the complex mineral silicates, and suggests the way in which silicic acids may condense to produce silica, which may thus be a complex mixture of different polymers. No closed chain compound has yet been obtained, however, containing in its molecule more than four atoms of silicon and four of oxygen.<sup>2</sup>

Having regard to the way in which natural silicates have crystallised from molten magmas, Mendeleef has likened their formation, whether produced naturally, as for example in granites and lavas, or artificially, as in slags and glasses, to that of alloys, from which definite compounds of the constituent metals crystallise.

The earliest classification of the natural silicates, that of Berzelius, was purely empirical, and was upon a dualistic basis. Recognising that silicates are compounds of silica with other oxides, more or less basic, Berzelius employed the oxygen ratio as a means of classification. An example will make this clear.



This method is not satisfactory, since it separates silicates that are naturally allied. For example, albite and anorthite are isomorphous feldspars, but they are separated in Berzelius's system, thus:



This raises the question whether or not alumina should be regarded as basic in such silicates—a question which will be dealt with later.

A more modern method of classification consists in formulating a number of hypothetical silicic acids and arranging the natural silicates in groups according to these types. In this way a large number of silicates can be brought together under a few types.

<sup>1</sup> Kipping, *Trans. Chem. Soc.*, 1912, 101, 2108, 2112.

<sup>2</sup> Meads and Kipping, *Trans. Chem. Soc.*, 1915, 107, 459.

The following are these types, with a few examples of each :

#### MONOSILICATES

##### I. Orthosilicic acid Type, $\text{H}_4\text{SiO}_4$ or $\text{Si}(\text{OH})_4$ .

Olivine . . .	$\text{Mg}_2\text{SiO}_4$ .
Willemite . . .	$\text{Zn}_2\text{SiO}_4$ .
Anorthite . . .	$\text{CaAl}_2(\text{SiO}_4)_2$ .
Garnet . . .	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ .

##### II. Metasilicic acid Type, $\text{H}_2\text{SiO}_3$ or $\text{SiO}(\text{OH})_2$ .

Wollastonite . . .	$\text{CaSiO}_3$ .
Leucite . . .	$\text{KAl}(\text{SiO}_3)_2$ .
Enstatite . . .	$\text{MgSiO}_3$ .
Beryl . . .	$\text{Gl}_3\text{Al}_2(\text{SiO}_3)_6$ .

#### DISILICATES

##### III. Orthodisilicic acid Type, $\text{H}_6\text{Si}_2\text{O}_7$ or $(\text{HO})_3\text{Si}-\text{O}-\text{Si}(\text{OH})_3$ .

Barysilite . . .	$\text{Pb}_2\text{Si}_2\text{O}_7$ .
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##### IV. Metadisilicic acid Type, $\text{H}_2\text{Si}_2\text{O}_5$ or $\text{HOOSi}-\text{O}-\text{SiOOH}$ .

Titanite . . .	$\text{CaSiTiO}_5$ .
Petalite . . .	$\text{LiAl}(\text{Si}_2\text{O}_6)_2$ .

#### TRISILICATES

##### V. Orthotrisilicic acid Type, $\text{H}_8\text{Si}_3\text{O}_{10}$ or

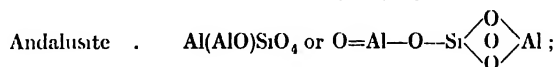
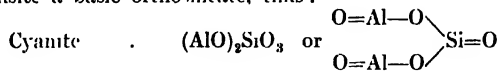
	$(\text{HO})_3\text{Si}-\text{O}-\text{Si}(\text{OH})_2-\text{O}-\text{Si}(\text{OH})_3$ .
Melhlith . . .	$\text{Ca}_4\text{Si}_3\text{O}_{10}$ .

##### VI. Trisilicic acid Type, $\text{H}_4\text{Si}_3\text{O}_8$ or $(\text{HO})_2\text{Si} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Si} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Si}(\text{OH})_2$ .

Orthoclase . . .	$\text{KAlSi}_3\text{O}_8$ .
Albite . . .	$\text{NaAlSi}_3\text{O}_8$ .

A large number of natural silicates can be included in the above classes, and so far the system seems satisfactory. There are, however, some important silicates that appear not to conform to any of these types, prominent among which are cyanite and andalusite, both of which possess the composition  $\text{Al}_2\text{SiO}_5$ , and kaolinite, or china clay, which is  $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ , to which serpentine,  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ , corresponds.

It is usual, however, to consider cyanite a basic metasilicate and andalusite a basic orthosilicate, thus :

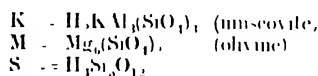


whilst kaolinite and serpentine are hydrated forms of orthodisilicates,  $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  and  $\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  respectively.  $\text{Al}_2\text{SiO}_5$  has been prepared artificially by Shepherd, Rankin, and Wright,<sup>1</sup> but it is identical with the mineral sillimanite, into which andalusite and cyanite are successively transformed when they are heated above 1300° C.

The micas are, moreover, an important class of natural silicates which appear not to come within any of the above categories. They

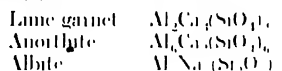
<sup>1</sup> Shepherd, Rankin, and Wright, *Amer. J. Sci.*, 1909, [iv], 28, 293

are regarded by F. W. Clarke<sup>1</sup> as derivatives, or isomorphous mixtures of derivatives, of the aluminous silicates  $\text{Al}_3(\text{SiO}_3)_3$  and  $\text{Al}_4(\text{Si}_3\text{O}_8)_3$ , and therefore as belonging to the orthosilicic or trisilicic type. Muscovite, for example, which occurs in granite, is  $\text{H}_2\text{KAl}_3(\text{SiO}_3)_3$ . Tschermak, however, supposes the mica, to consist of isomorphous mixtures of three types of molecules symbolised respectively by K, M and S thus:



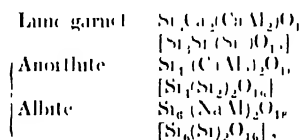
It will be observed that S introduces an additional type of silicic acid molecule.

These considerations suffice to show that the classification of the natural silicates is a matter of great complexity, and that to refer them to a few types of hypothetical silicic acids constructed *a priori* on theoretical grounds is not to account for them completely. Especially is it to be noted that this chemical classification is not the kind of classification which would be evolved by a mineralogist who took account of natural relationships. It has already been pointed out that classification by oxygen ratio separates albite and anorthite, which are naturally allied; chemical classification according to types of silicic acid also separates them. Clarke, by classifying natural silicates as derivatives of  $\text{Al}_3(\text{SiO}_3)_3$ , gives the following formulae:



but this arrangement brings together garnet and anorthite, which are dissimilar, and still separates anorthite and albite which are similar in physical properties.

According to the system of Goldschmidt, silicates may be derived from polymerised silica molecules such as  $\text{Si}_6\text{O}_{18}$  or  $\text{Si}_8\text{O}_{26}$  by the replacement of silicon atoms by equivalent metallic or other atoms. Thus these three silicates are formulated:



and the system has the merit of classifying anorthite and albite together and separating them from garnet.

The natural silicates may now be considered from another point of view. It will have been observed that a large number of them contain alumina, an amphoteric oxide possessing distinctly acidic properties which are shown in the existence of aluminates, of which the spinels, e.g.  $\text{MgAl}_2\text{O}_4$ , are natural examples. Thus alumina approaches silica in chemical properties, with which indeed in the crystalline form, it is isomorphous. Consequently it cannot be accurate to regard alumina as entirely a basic oxide in the aluminous silicates, and so several other

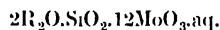
<sup>1</sup> Clarke, *Amer. J. Sci.* 1889, [m], 38, 384.

points of view present themselves,<sup>1</sup> which can be stated in the form of three distinct theories :

(1) The aluminous silicates are of the nature of double salts analogous to the alums, aluminum silicate and a silicate of a stronger base than alumina being united together by a kind of residual affinity whose strength depends upon the difference in basic power between alumina and the other metallic oxide, just as the union of sulphates in the alums depends upon such a difference.

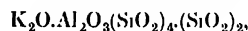
(ii) The aluminous silicates are isomorphous mixtures of silicates and aluminates.

(iii) The aluminous silicates are salts of strongly basic radicles with complex silico-alumic acids, which are analogous to the complex acids formed by molybdenum and tungsten—such as, for example, the silicomolybdate<sup>2</sup>

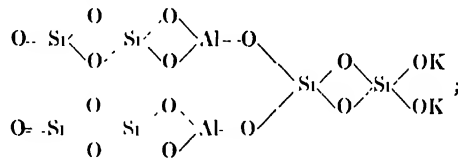


It is doubtful, however, whether alumina forms complex acids analogous to those of the trioxides of the sixth group; rather will it take the place of silica itself in such a compound as the above. Nevertheless various attempts have been made to express the constitution of the aluminous silicates on the assumption that they are individual compounds and not isomorphous mixtures. Orthoclase feldspar, perhaps the most important of these compounds, will serve as an example.

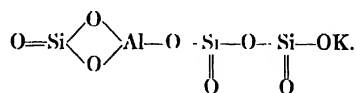
Tschermak<sup>3</sup> writes the formula for orthoclase thus :



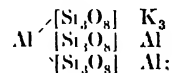
and constitutionally :



whilst P. Groth,<sup>4</sup> adopting the simplest empirical formula, represents the silicic acid to be entirely in the meta- form, thus :



Clarke, in accordance with his theory that aluminous silicates are derivatives of aluminum silicates, formulates feldspar thus :



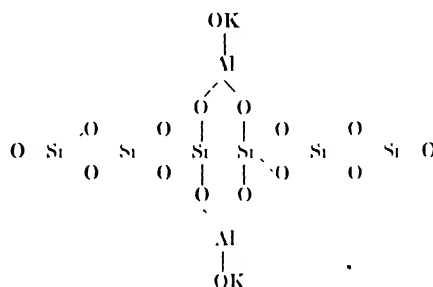
<sup>1</sup> Vide W. and D. Asch *The Silicate* (Julius Springer, Berlin, 1911), for an exhaustive treatment of the subject

<sup>2</sup> W. Asch, *Dissertation*, Berlin, 1901

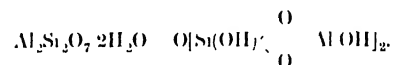
<sup>3</sup> Tschermak, *Monatsh. Mitt.*, 1871, 2 Hefte

<sup>4</sup> P. Groth, *Tabellarische Übersicht d. Mineralien*, 14 Aufl., S. 120, Braunschweig, 1898.

and Vernadsky,<sup>1</sup> considering this silicate to be the potassium salt of the complex silico-aluminate acid  $H_2O \cdot Al_2O_3 \cdot 6SiO_2$ , develops its structural formula thus:

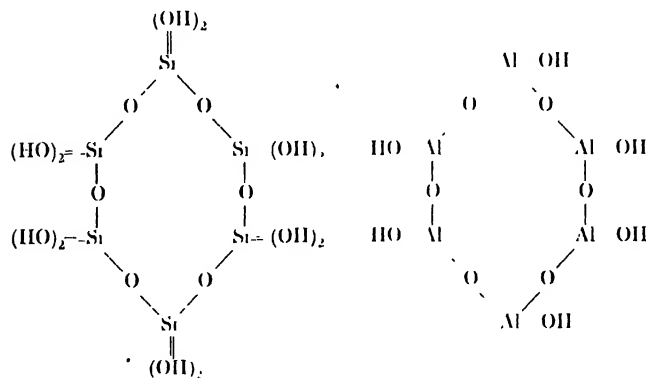


Clay, moreover, is believed by Loew to be an anhydrosilico-aluminate acid, thus <sup>2</sup>:



The subject is carried much further in the *hexite-pentite theory* of W. and D. Asch <sup>3</sup>.

According to this theory silica and alumina form closed chains containing 6 or 5 atoms of silicon or aluminum alternated with oxygen atoms. The hydrated forms of silica and alumina hexite are:

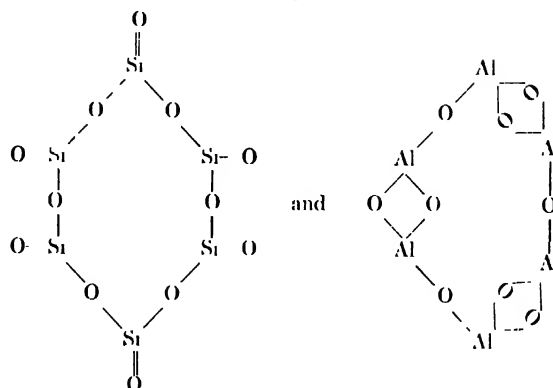


<sup>1</sup> Vernadsky, *Zeitsch. Krist. Min.*, 1901, 34, 61.

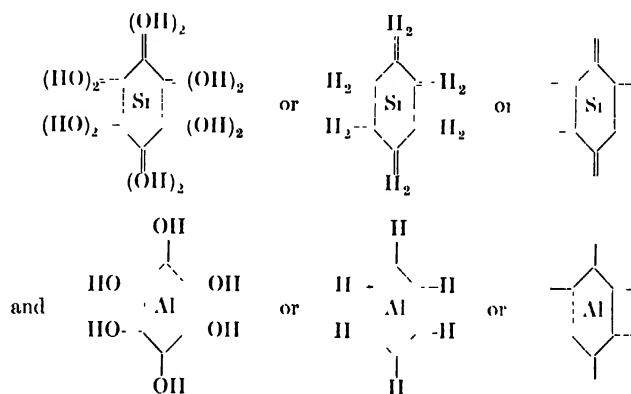
<sup>2</sup> Loew, *Chem. Zentr.*, 1911, [u] 128, from *Landw. Jahrb.*, 46, 161.

<sup>3</sup> W. and D. Asch *loc. cit.*

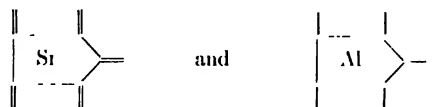
to which there correspond the anhydrides :



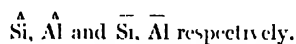
The hydrohexites are represented more briefly thus



Similarly the silica and alumina pentites are, in their abbreviated form :

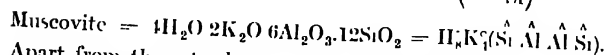
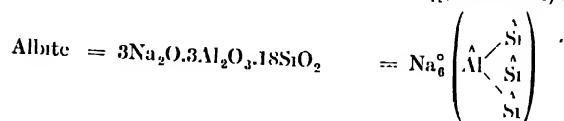
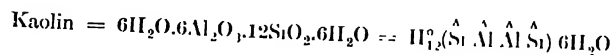
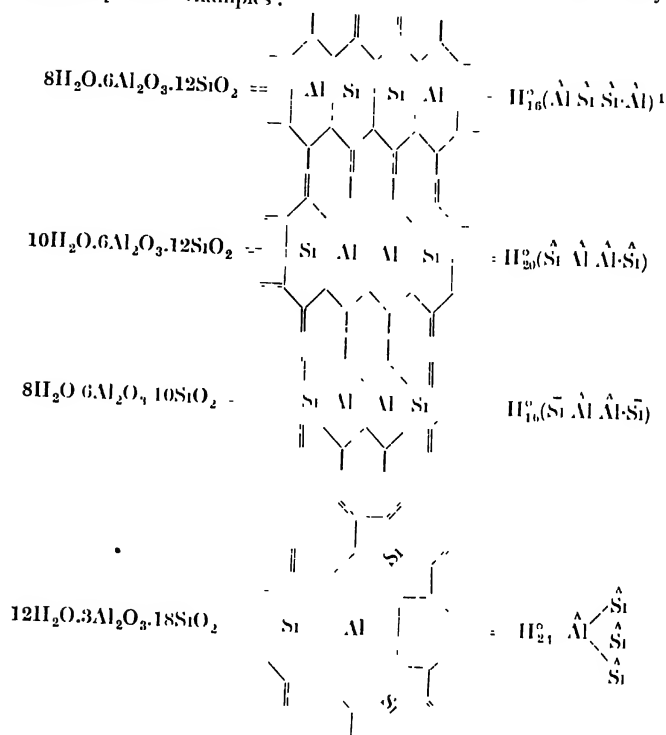


whilst the hexite and pentite symbols in their briefest form are :



The fundamental assumption of the theory of W. and D. Aesch is that all the natural silicates contain ten- or twelve-membered rings of alternate silicon or aluminum and oxygen atoms, and by means of this theory

a very large number of silicates can be formulated. This may be shown by a few examples:



Apart from theoretical views upon the constitution of the natural silicates, these minerals may be practically divided into two great classes: *anhydrosilicates* and *hydrosilicates* or *zeolites*<sup>2</sup> respectively. The former silicates contain no combined water, and are decomposed only by prolonged heating with concentrated sulphuric acid, or, better,

<sup>1</sup> H<sup>o</sup> = (HO). The symbols Si, Si<sup>o</sup>, etc., have been explained on the previous page.

<sup>2</sup> Zeolite = boiling stone *ζῆον*, to boil.



by fusion with excess of alkali carbonate. Hydrosilicates intumescence when heated before the blowpipe, with loss of water, and are decomposed by concentrated hydrochloric acid with separation of gelatinous silica. Their hardness (3.5 to 5) is considerably less than that of the anhydrosilicates (4.5 to 7), and this, together with their greater reactivity, shows them to have a molecular texture less dense than that of the anhydrosilicates.

Many examples of anhydrosilicates have already been given; a few typical hydrosilicates are:

Natrolite	.	$\text{H}_2\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{12}$	.	rhombic
Chabazite	.	$\text{H}_8\text{CaAl}_2\text{Si}_4\text{O}_{16} \cdot 2\text{H}_2\text{O}$	.	rhombohedral
Phillipsite	.	$\text{H}_2\text{CaAl}_2\text{Si}_5\text{O}_{16} \cdot 4\text{H}_2\text{O}$	.	monoclinic
Stilbite	.	$\text{H}_4\text{CaAl}_2\text{Si}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$	.	monoclinic.

The constitution of numerous natural silicates has been investigated by Tschermak<sup>1</sup> in the following manner: The powdered silicate was decomposed by prolonged digestion with concentrated hydrochloric acid at a temperature approaching 60° C.; the liberated silicic acid was thoroughly washed, and then allowed to dry slowly in the air. The rate at which loss of weight proceeded was found to change at a certain point which was believed to indicate transition from aqueous evaporation to dehydration; and the composition of the silicic acid at this point was supposed to correspond to that of the mineral which was a salt of the acid. Thus, for example, whilst the hydrolysis of silicon tetrachloride yielded orthosilicic acid,  $\text{H}_2\text{SiO}_4$ , of density 1.576, the same acid was obtained from natrolite,  $\text{Na}_2\text{H}_4\text{Al}_2\text{Si}_3\text{O}_{12}$ , and from diopside,  $\text{H}_2\text{CaSiO}_4$ , which are consequently orthosilicates. Hemimorphite,  $\text{H}_2\text{ZnSiO}_4$ , also, in spite of its empirical formula, is shown to be an orthosilicate by this method; whilst anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , yields metasilicic acid,  $\text{H}_2\text{SiO}_3$  (density 1.813), and leucite,  $\text{KAlSi}_3\text{O}_8$ ,  $\text{H}_4\text{Si}_2\text{O}_6$ , or "leucite" acid, a polymer of metasilicic acid, of density 1.809. "Garnet" acid,  $\text{H}_2\text{Si}_3\text{O}_9$ , has the density 1.910 and "albite" acid,  $\text{H}_2\text{Si}_3\text{O}_9$ , the density 2.043. The different acids are distinguished by their behaviour towards methylene blue. The conclusions of Tschermak have been adversely criticised by Muggge.<sup>2</sup>

The preparation of artificial silicates, corresponding to the natural minerals, by fusing together their constituents is a method of study which has been pursued by Vogt,<sup>3</sup> and by Doelter and his pupils.

Vogt applies the principles of physical chemistry to the crystallisation of silicates from fused magmas, and especially the conclusions of Roozeboom concerning the solidifying-points of mixed crystals. Consequently he believes that the identity of the silicates is preserved in the fused state, and that their molecular weights may be determined from the depression of the freezing-points of the molten magmas. Doelter,<sup>4</sup> on the other hand, who has determined the melting-points of a large number of silicates, regards them as highly dissociated in the liquid state, and dissents from some of Vogt's conclusions.

<sup>1</sup> Tschermak, *Zeitsch. physikal. Chem.*, 1905, 53, 349.

<sup>2</sup> Muggge, *Contrib. Min.*, 1908, 129, 325; see also Lebedeff, *Zeitsch. anorg. Chem.*, 1911, 70, 301.

<sup>3</sup> Vogt, *Die Silikatschmelzungen*, Christiansia, 1903; Tschermak, *Mineralogische Mitteilungen*, 1906, 24, 437, and 1907, 25, 361.

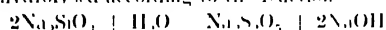
<sup>4</sup> Doelter, *Sitzungsber. K. Akad. Wiss. Wien*, 1904, 113, [1], 177.

A number of "hydrothermal" silicates have been prepared by Baur and Becke<sup>1</sup> by heating amorphous silica, alumina, and lime with sodium or potassium hydroxide to 350–450° C. in a steel cylinder closed with a steel screw. The following are among the "minerals" so obtained: quartz, opal, orthoclase, albite, oligoclase, and diopside, muscovite.

Few definitely crystallised artificial silicates exist, and these are confined to the alkali metals.

**Sodium Metasilicate** may be obtained by inoculating its strongly alkaline solution with the solid salt, and when recrystallised from warm 2–3 per cent. solution of sodium hydroxide yields rhombic crystals having the composition  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ . These crystals melt at 48° C., and slowly lose six molecules of water when kept over sulphuric acid. The trihydrate  $\text{Na}_2\text{SiO}_3 \cdot 3\text{H}_2\text{O}$  thus obtained yields the hexahydrate  $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$  when allowed to stand over 25 per cent. sodium hydroxide solution. High temperature is necessary for the complete dehydration of the salt.<sup>2</sup>

The aqueous solution of this salt is strongly alkaline, and is believed to have been hydrolysed according to the reaction<sup>3</sup>



A dilute aqueous solution of sodium silicate may be titrated with decormal acid as if it were sodium hydroxide when methyl orange is used as indicator.

In commercial sodium silicate the ratio by weight of silica to soda may be as high as 3 to 1. When the proportion of silica is large the silicate dissolves only very imperfectly in much water.

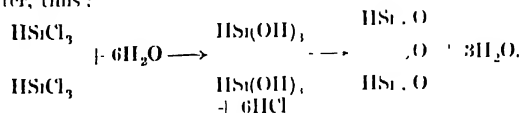
### SILICON OXYHYDRIDES

Several compounds exist containing more than one silicon atom combined with both oxygen and hydrogen. The three whose compositions are definitely known are:

Silicoformic anhydride	$\text{H}_2\text{Si}_2\text{O}_4$
Silico-oxalic acid	$\text{H}_4\text{Si}_2\text{O}_5$
Silicomalic-oxalic acid	$\text{H}_4\text{Si}_2\text{O}_6$

These names suggest analogous carbon compounds, and the latter two correspond, at least in empirical composition, to oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , and mesoxalic acid,  $\text{H}_3\text{C}_3\text{O}_6$ .

**Silicoformic Anhydride**,  $\text{H}_2\text{Si}_2\text{O}_4$ , was obtained in an impure form by Bufl and Wohler,<sup>4</sup> and pure by Friedel and Ladenburg,<sup>5</sup> by decomposing silicochloroform with ice-cold water. The formation of the anhydride is probably preceded by that of the free acid, which then loses water, thus:



<sup>1</sup> Baur and Becke, *Zeitsch. anorg. Chem.*, 1911, 72, 119.

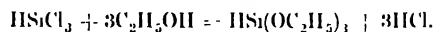
<sup>2</sup> Vesterberg, *Zeitsch. anorg. Chem.*, 1914, 88, 311.

<sup>3</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1893, 12, 773; Hantzsch, *Zeitsch. anorg. Chem.*, 1902, 30, 295; Mylius and Groschuff, *Ber.*, 1906, 39, 116.

<sup>4</sup> Bufl and Wohler, *Annalen*, 1857, 104, 101.

<sup>5</sup> Friedel and Ladenburg, *Annalen*, 1867, 143, 121.

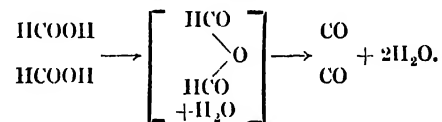
Although orthosilicoformic acid is unstable, its ethyl ester is formed by the action of alcohol on silicochloroform, thus :



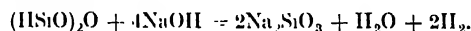
For the less reactive chloroform to yield the corresponding orthoformic ester, sodium ethoxide must be employed thus :



Formic anhydride,  $(\text{HCO})_2\text{O}$ , corresponding to  $(\text{HSiO})_2\text{O}$ , is unknown, for any attempt to dehydrate formic acid yields carbon monoxide :



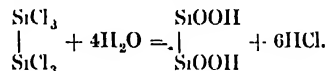
Silicoformic anhydride is an insoluble white powder, which should be dried *in vacuo* over sulphuric acid. It may be heated to  $300^\circ \text{C}$ . without decomposition, but at a higher temperature it evolves water and silicene,  $\text{SiH}_4$ , and leaves a residue of silica. It inflames when heated to a high temperature in the air, and emits a phosphorescent light; it is stable towards acids, but reacts with alkalis, forming silicates and hydrogen, thus, *e.g.* :



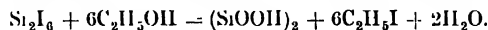
Towards various substances in solution it behaves as a reducing agent; thus it reduces permanganic and chromic acids, and separates sulphur from sulphurous acid, and mercury, silver, gold, and platinum from their salts.

These reducing properties are traceable to the hydrogen atom in silicochloroform, which persists in silicoformic anhydride. Like silicic acid, which it somewhat resembles in physical properties, this compound no doubt consists of polymerised molecules,  $(\text{H}_2\text{Si}_2\text{O}_3)_n$ .

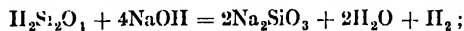
**Silico-oxalic Acid**,  $(\text{H}_2\text{Si}_2\text{O}_4)_n$ .—This compound, the silicon analogue of oxalic acid, is formed by the hydrolysis of hexachlorosilico-ethane,  $\text{Si}_2\text{Cl}_6$ , or hexa-iodosilico-ethane,  $\text{Si}_2\text{I}_6$ , by means of ice-cold water :



Hexa-iodosilico-ethane also reacts with absolute alcohol thus :

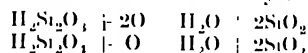


Silico-oxalic acid is conveniently prepared<sup>1</sup> by allowing moist air to act slowly upon hexachlorosilico-ethane contained in a platinum capsule cooled by ice, and then washing the product with cold water till it is free from chloride, and drying it in a vacuum. It is a white insoluble powder which explodes feebly when heated or rubbed. It dissolves in alkalis, forming silicates with evolution of hydrogen, thus :



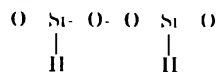
<sup>1</sup> Gattermann and Weinlg, *Ber.*, 1894, 27, 1942

consequently it is a reducing agent; it reduces permanganic acid quickly, and chromic acid slowly, but does not precipitate gold from cold solution. That silico-oxalic acid possesses but half the reducing power of silicoformic anhydride is indicated by the equations:

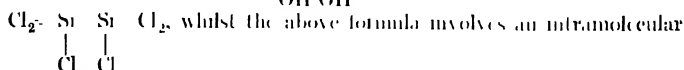


The name silico-oxalic acid is hardly justifiable since this substance forms no salts.

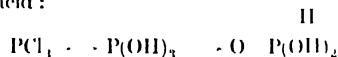
As regards the constitution of this compound, the formula  $(\text{SiOOH})_2$  postulates reducing properties allied to those of  $(\text{COOH})_2$ , nevertheless it has been proposed to formulate this substance thus<sup>1</sup>:



Now the formula  $\begin{array}{c} \text{O} \quad \text{Si} \quad \text{Si} \quad \text{O} \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$  is derivable directly from

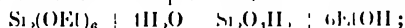


whilst the above formula involves an intramolecular change, for which some analogy appears to be provided, for instance by phosphorous acid:

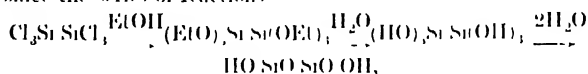


The cases, however, are not parallel for in the latter example the valency of the phosphorus atom is increased. Moreover, there is serious objection to assuming an oxygen chain to be present in the molecule of silico-oxalic acid, and no objection to retaining the formula analogous to that of oxalic acid.

Further, it has been shown by Martin<sup>2</sup> that silico-oxalic acid is produced, in a yield of 99-100 per cent., by the reaction:



and since the series of reactions:



proceeds quantitatively, this fact affords additional evidence that the constitution of silico-oxalic acid is analogous to that of oxalic acid. The compound is, however, probably a polymer with a cyclic constitution, as appears below.

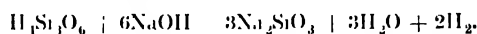
**Silicomes-oxalic Acid,  $\text{H}_4\text{Si}_2\text{O}_6$**  This compound, which is the silicon analogue of mesoxalic acid:



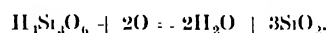
<sup>1</sup> Grossmann, see Abegg, *Handbuch der anorg. Chem.*, III, ii, 354<sup>4</sup>

<sup>2</sup> Martin, *Trans. Chem. Soc.* 1915, 107, 319

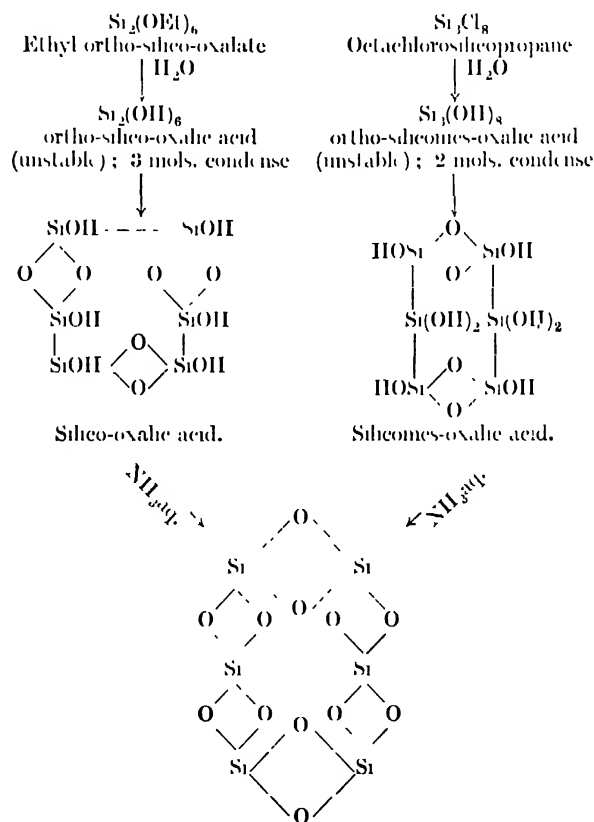
is formed by the action of moist air on octachlorosilicopropane,  $\text{Si}_3\text{Cl}_8$ , at  $0^\circ\text{C}$ . It is a white unstable powder, which is insoluble in water, but reacts with alkali forming silicate and hydrogen :



It possesses reducing properties, indicated thus :



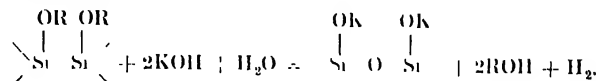
Silico-oxalic acid and silico-silico-oxalic acid yield identical forms of silica when treated with ammonia, and Martin<sup>1</sup> accounts for this fact by the following scheme, in which the polymerised and cyclic constitution of these two acids is set forth :



When ethyl ortho-silico-oxalate (hexa-ethoxysilico-ethane) is treated with sodium or potassium hydroxide solution, hydrogen is evolved, and

<sup>1</sup> Martin, *Trans. Chem Soc.*, 1915, 107, 1043

a silicate formed by the interpolation of an oxygen atom between the two silicon atoms thus

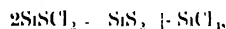


## SILICON AND SULPHUR

The following silicon compounds containing sulphur are known

Silicon disulphide	•	•	•	SiS <sub>2</sub>
Silicon monosulphide	•	•	•	SiS
Silicon oxysulphide	•	•	•	SiOS
Silicon thiochloride	•	•	•	SiS <sub>2</sub> Cl <sub>2</sub>
Silicon thiobromide	•	•	•	SiS <sub>2</sub> Br <sub>2</sub>
Silicon chlorohydrosulphide	•	•	•	SiCl <sub>3</sub> SH
Silicothio-urea	•	•	•	SiS(NH <sub>2</sub> ) <sub>2</sub>

**Silicon Disulphide**, SiS<sub>2</sub>, can be prepared by passing the vapour of carbon disulphide over a heated mixture of silica and carbon, but is best obtained by heating to a red heat an intimate mixture of amorphous silicon with three times its weight of powdered sulphur, and subliming the product under reduced pressure.<sup>1</sup> It is also formed by the dry distillation of the thiochloride



and by adding lithium silicide to molten sulphur.<sup>2</sup>

Silicon disulphide forms white silky needles, which may be sublimed in an inert atmosphere, but which burn to silica and sulphur dioxide when heated in air. Moisture decomposes this compound, forming silica and hydrogen sulphide; chlorine forms chlorides of sulphur and silicon; fused sodium sulphide yields sodium thiosilicate, Na<sub>2</sub>SiS<sub>3</sub>,<sup>3</sup> so that silicon disulphide, SiS<sub>2</sub>, is thiosilicic anhydride.

**Silicon Monosulphide**, SiS, is formed, together with the oxysulphide, SiOS, when sulphur vapour is passed over silicon heated to whiteness in a porcelain tube,<sup>4</sup> and also when ferrosilicon and sulphur are heated together in an electric furnace.<sup>5</sup> Silicon monosulphide is a yellow volatile solid, which also appears to exist in a black modification, and dissolves in alkali solution with evolution of hydrogen.

**Silicon Oxysulphide**, SiOS, appears to be a yellow solid which dissolves in alkali without evolution of hydrogen.

**Silicon Thiochloride**, SiS<sub>2</sub>Cl<sub>2</sub>, is formed, together with silicon disulphide and silicon tetrachloride, when the vapour of sulphur monochloride reacts with crystallised silicon at a red heat.<sup>6</sup> The product is purified by crystallisation from carbon tetrachloride, and sublimed at 100° C. in a stream of dry air. It has also been prepared by the pro-

<sup>1</sup> Hempel and von Haasy, *Zeitsch. anorg. Chem.*, 1900, 23, 32

<sup>2</sup> Moissan, *Compt. rend.*, 1902, 134, 1093

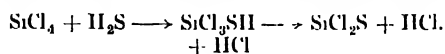
<sup>3</sup> Hempel and von Haasy, *ibid.*

<sup>4</sup> Colson, *Bull. Soc. chim.*, 1882, [n], 38, 56; Rankin and Rivington, *Proc. Chem. Soc.*, 1908, 24, 131.

<sup>5</sup> Cambi, *Atti R. Accad. Lincei*, 1910, [v], 19, n, 294, 1911, [v], 20, i, 433

<sup>6</sup> Beeson, *Compt. rend.*, 1891, 113, 1040.

longed interaction of silicon tetrachloride vapour and hydrogen sulphide at a dull red heat, when the following changes take place<sup>1</sup>:

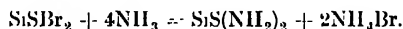


This compound crystallises from carbon disulphide in colourless prisms which melt at 74° C. (Besson) or 75° C. (Blx and Wirbelauer); the liquid boils at 92° C. under 22.5 mm. pressure (Blx and Wirbelauer). Water and moist air decompose silicon thiochloride with evolution of hydrogen chloride and sulphide and separation of silicic acid; while heat breaks it up into silicon tetrachloride and disulphide.

**Silicon Thiobromide, SiSBr<sub>2</sub>**, is formed with evolution of hydrogen bromide by the interaction of silicon tetrabromide and hydrogen sulphide at 150° C. in presence of aluminum bromide as a catalyst.<sup>2</sup> It is separated from unchanged silicon tetrabromide by fractionation *in vacuo*, and forms colourless plates melting at 93° C. to a liquid which boils at 150° C. under 18.3 mm. pressure. The crystals fume in moist air, and react vigorously with water, with separation of silicic acid and evolution of hydrogen bromide and sulphide.

**Silicon Chlorohydrosulphide, SiCl<sub>3</sub>SH.**—It has been seen under silicon thiochloride that silicon chlorohydrosulphide is an intermediate product of the interaction of silicon tetrachloride and hydrogen sulphide. This compound is therefore formed by passing a mixture of silicon tetrachloride vapour and hydrogen sulphide through a tube at a lower temperature than that required for preparing silicon thiochloride.<sup>3</sup> It is separated from unchanged silicon tetrachloride by fractional distillation and condensation in a freezing mixture. It is a colourless, fuming liquid, of density 1.43 at 15° C., which boils at 96° C. Friedel and Ladenburg<sup>4</sup> found its vapour density between 155° C. and 161° C. to be 5.74 and 5.24–5.32, theory requiring 5.83 (an = 1). It is decomposed by water with separation of silicic acid and evolution of hydrogen chloride and sulphide; bromine forms hydrogen bromide and SiCl<sub>3</sub>Br, and alcohol the compound Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SH.

**Silicothio-urea, SiS(NH<sub>2</sub>)<sub>2</sub>**.—This compound is formed by the action of ammonia on silicon thiobromide by a reaction analogous to that by which the corresponding carbon compound is formed:



Silico-urea is not known, for no simple silicon oxyhalide, SiOX<sub>2</sub>, exists from which it could be prepared.

Silicothio-urea differs from its carbon analogue in being decomposed by water; hence the reaction for its preparation is carried out in anhydrous solution, as follows: Silicon thiobromide is dissolved in benzene, and dry ammonia is passed into the solution at low temperature, when silicothio-urea separates, together with ammonium bromide. Liquid ammonia is employed to dissolve the latter, and the silicothio-urea then remains as a white powder, which slowly decomposes at atmospheric temperature, evolving ammonia and hydrogen sulphide

<sup>1</sup> Blx and Wirbelauer, *Ber.*, 1903, 36, 4220.

<sup>2</sup> Blx, *Ber.*, 1903, 36, 4218.

<sup>3</sup> Pierre, *Ann. Chim. Phys.*, 1848, [iii], 24, 286.

<sup>4</sup> Friedel and Ladenburg, *Ann. Chim. Phys.*, 1872, [iv], 27, 416.

Water hydrolyses this compound into silicic acid, ammonia, and hydrogen sulphide. It possesses feebly basic properties, and forms salts with the halogen hydrides.

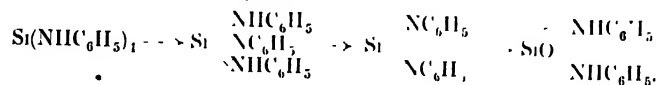
## SILICON AND SELENIUM

**Silicon Selenide**,  $\text{SiSe}_2$ , formed by the action of hydrogen selenide gas on crystalline silicon at a red heat,<sup>1</sup> is a hard, metallic-looking solid with a penetrating smell, which is decomposed by water into silicic acid and hydrogen selenide.

## SILICON AND NITROGEN

The compounds which contain carbon atoms linked with those of nitrogen are exceedingly numerous and important, and the extent of the resemblance between carbon and silicon may be partly judged by a comparison of the nitrogenous silicon compounds with those of carbon. Very few nitrogenous compounds of silicon exist, however; and those that are known show little relationship with corresponding carbon compounds.

Reynolds<sup>2</sup> nevertheless has drawn attention to the following reactions of orthosilicic amide which are analogous to those of the corresponding carbon compound:

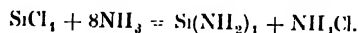


The following are the organic compounds which contain linkages of silicon and nitrogen atoms:

Silicon tetramide . . . . .	$\text{Si}(\text{NH}_2)_4$
Silicon di-imide . . . . .	$\text{Si}(\text{NH})_2$
Silicon nitride, or siheam . . . . .	$\text{Si}_2\text{N}_4\text{H}_4$
Siliconnitrogen hydride . . . . .	$\text{HSi}-\text{N}$
Silicon nitride . . . . .	$\text{Si}_2\text{N}_4(\text{SiN.Si}_2\text{N}_3)$

There exist also silicon carbonitride,  $\text{Si}_2\text{C}_2\text{N}$ , and silicothio-urea  $\text{SiS}(\text{NH}_2)_2$ , previously noticed.

**Silicon Tetramide**,  $\text{Si}(\text{NH}_2)_4$ , is prepared by the general method for preparing amides, that is, by the interaction of the acid chloride and ammonia. Thus when silicon tetrachloride and ammonia interact in benzene solution<sup>3</sup> below  $0^\circ \text{C}$ ., or when liquid ammonia and the tetrachloride are mixed together<sup>4</sup> below  $0^\circ \text{C}$ ., a white solid is formed which is a mixture of the tetramide and the necessary by-product, ammonium chloride:



From this mixture liquid ammonia dissolves ammonium chloride, leaving silicon tetramide as an unstable, amorphous white substance which above  $0^\circ \text{C}$ . loses ammonia, passing into the di-imide. Water decomposes the tetramide into silicic acid and ammonia.

<sup>1</sup> Sabatier, *Compt. rend*, 1891, 113, 132

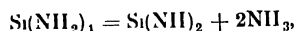
<sup>2</sup> Reynolds, *Trans. Chem. Soc.*, 1889, 55, 471, 1900, 77, 836, 1905, 87, 1870

<sup>3</sup> Lengfield, *Amer. Chem. J.*, 1899, 21, 531

<sup>4</sup> Vigouroux and Hugot, *Compt. rend*, 1903, 136, 1670



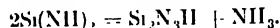
**Silicon Di-imide**,  $\text{Si}(\text{NH})_2$ , is formed from the tetramide by loss of ammonia<sup>1</sup>:



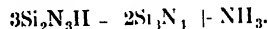
which commences above 0° C. and is complete at 120° C. It is also produced by the action of liquid ammonia on silicon disulphide or thiochloride, and may be isolated from the product of the action of gaseous ammonia on silicon tetrachloride.<sup>2</sup>

Silicon di-imide is a white, infusible, amorphous powder, stable towards moderate heat in absence of air; it is basic, forming the white hydrochloride  $\text{Si}(\text{NH})_2 \cdot 2\text{HCl}$ . Water hydrolyses it to silicic acid and ammonia.

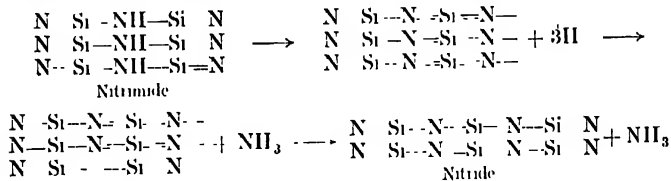
**Silicon Nitrimide** (*Silicam*),  $\text{Si}_2\text{N}_3\text{H}$ .—Although silicon di-imide can be heated gently in an inert atmosphere without decomposition, it loses ammonia when heated in nitrogen to 900° C., yielding the nitrimide, a substance of unknown constitution, thus<sup>3</sup>:



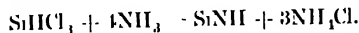
The product is an amorphous powder, stable towards water. When it is heated to 1200–1300° C. it loses the hydrogen remaining in it as ammonia, and leaves a residue of nitride, thus:



Making certain assumptions as to the constitution of the nitrimide and nitride, this change may be represented tentatively as follows:



**Siliconitrogen Hydride**,  $\text{SiNH}$ .—This compound, which is the silicon analogue of hydrocyanic acid, is formed by the action of ammonia on silicochloroform vapour<sup>4</sup>:



The gases are diluted with hydrogen and cooled to prevent a too vigorous reaction, and moisture and air are rigorously excluded to prevent hydrolysis or oxidation of the product. Ammonium chloride is removed from the mixture by means of liquid ammonia, but the hydride has not been obtained pure.

Siliconitrogen hydride is a white powder which sublimes with decomposition at 300° C. under reduced pressure. It reacts with water<sup>5</sup> to form silicic acid or a silicate, ammonia and hydrogen:



<sup>1</sup> and Hugot, *Compt. rend.*, 1903, 136, 1670.

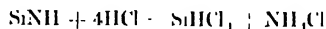
<sup>2</sup> Vicker, 1889, 22, 218. <sup>3</sup> Ruff and Wirbelauer, *Ber.*, 1903, 36, 4220.

<sup>4</sup> Gatterer, *ibid.*, 1841.

<sup>5</sup> Blunt, *ibid.*, 1841.

<sup>6</sup> Ruff and Wirbelauer, 1905, *Ber.*, 38, 1000.

it is consequently a strong reducing agent, and in this respect resembles silicoformic anhydride. Dry hydrogen chloride gas regenerates silicochloroform, thus:



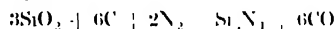
Evidently silicoutrogen hydride does not resemble hydrogen cyanide.

**Silicon Nitrides.** Several nitrides of silicon appear to exist as white amorphous substances. They are

$\text{SiN}_2$	density 3.17,
$\text{Si}_2\text{N}_3$	3.61, insoluble in $\text{HF}$ ,
$\text{Si}_3\text{N}_4$	3.44, soluble in $\text{HF}$ , forming $(\text{NH}_4)_2\text{SiF}_6$ .

and are produced together when silicon is strongly heated in nitrogen.<sup>1</sup> When silicon is heated in a crucible packed round with carbon, access of oxygen is almost prevented,<sup>2</sup> and  $\text{Si}_3\text{N}_4$  is formed together with the carbinitride  $\text{Si}_2\text{C}_2\text{N}$  (or  $\text{Si}_2\text{C}_3\text{N}$ ), the carbide  $\text{SiC}$  and the carboside  $\text{SiCO}$ .

According to Martignon,<sup>3</sup> the nitride  $\text{Si}_3\text{N}_4$  is formed when a mixture of silica and carbon is heated in a current of nitrogen at 1400–1500° C., according to the equation:



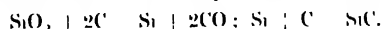
From theoretical considerations the heat of formation of this nitride is calculated to be 159 300 calories.

## SILICON AND CARBON

Silicon and carbon combine together at high temperature to form two compounds,  $\text{SiC}$  and  $\text{SiC}_2$ , the former of which is known in the crystalline and amorphous states.

The amorphous monocarbide,  $\text{SiC}$ , is prepared<sup>4</sup> by heating to a red heat in a bone-black crucible, surrounded with soot, a finely divided mixture of 1 part of crystallised silicon and 2 parts of silica. The product, which is green, is freed from the accompanying silica by means of hydrofluoric acid. A similar product is prepared commercially as a fireproof material called "Silundum."

**Crystalline Silicon Monocarbide (Carborundum),  $\text{SiC}$ .** The discovery of this important substance<sup>5</sup> by Acheson in 1891 was an outcome of the experiments of Moissan on the electric furnace. It may be prepared by fusing silicon with carbon,<sup>6</sup> or silica with calcium carbide,<sup>7</sup> in an electric furnace, or by the combination of carbon and silicon vapours produced therein. It is manufactured, however, by heating together in an electric furnace, built of firebrick and provided with carbon terminals, a mixture of coke, silica, salt, and sawdust. The water-power of Niagara furnishes the energy. The reactions are:



<sup>1</sup> Weiss and Engelhardt, *Zeitsch. anorg. Chem.*, 1909, 65, 38.

<sup>2</sup> Deville and Wöhler, *Annalen*, 1859, 110, 248.

<sup>3</sup> Martignon, *Bull. Soc. chim.*, 1913, [iv] 13, 791.

<sup>4</sup> Schutzenberger, *Compt. rend.*, 1892, 114, 1089.

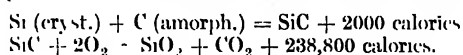
<sup>5</sup> For an account of the manufacture and properties of carborundum, see Kohn, *J. Soc. Chem. Ind.*, 1897, 16, 863.

<sup>6</sup> Moissan, *Compt. rend.*, 1893, 117, 425.

<sup>7</sup> Moissan, *Compt. rend.*, 1897, 124, 839.

The salt acts as a flux till it is volatilised, and the sawdust yields gaseous decomposition products which keep the mass porous. When the furnace is opened the carborundum is found surrounded with a zone of the less valuable amorphous monocarbide, formed at a lower temperature.

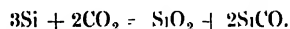
Carborundum crystallises in hexagonal plates of density 3.12. The crystals are lustrous, iridescent, and often translucent, and of a colour varying from sapphire blue to greenish brown. The hardness of this substance approaches that of diamond, being 9.5 on Moh's scale; so that it will scratch ruby. The heats of formation and combustion are respectively



Carborundum is practically unaltered by ignition at 1000° C. in air or oxygen. Neither hydrochloric nor sulphuric acid, nor even a mixture of hydrofluoric and nitric acids, attacks this substance; sulphur and fused nitre are without action upon it; chlorine decomposes it, slightly at 600° C., completely at 1200° C.; fused lead chromate oxidises it, and fused caustic alkali converts it into carbonate and silicate. Carborundum is used, on account of its excessive hardness, as an abrading, cutting, and polishing agent. It is employed in the iron and steel and other metal industries, and for smoothing pottery and polishing granite and glass. It is thus a substitute for emery.

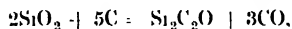
**Silicon Dicarbide,**  $\text{SiC}_2$ , was obtained by Colson<sup>1</sup> by passing ethylene, or hydrogen saturated with benzene vapour, over silicon heated to whiteness in a porcelain tube.

**Silicon Carboxide.**—The compound  $(\text{SiC})_x$  is formed when silicon is heated to whiteness in an atmosphere of carbon dioxide:



After the removal of silica with hydrofluoric acid the carboxide remains as a greenish white powder, which is stable towards alkalis.

A product called *Siloxicon* has been prepared by Colson,<sup>2</sup> and is manufactured by the Acheson Company at Niagara, by heating a mixture of sand, powdered coke, and sawdust in the electric furnace to a temperature not exceeding 2800° C. The reaction is approximately



but the product is a mixture, and may contain other bodies besides  $\text{Si}_2\text{C}_2\text{O}$ , e.g.  $\text{C}_7\text{Si}_7\text{O}$ , if the proportion of carbon to silica is varied. Siloxicon is refractory, and greyish green when cold, but light yellow above 300° F.; its density is 2.73, and it binds when ground with water and fired.<sup>3</sup>

## SILICON AND BORON

Two borides of silicon are known:  $\text{SiB}_3$  and  $\text{SiB}_6$ .<sup>4</sup> They are formed together when boron is heated with excess of crystallised silicon in an electric furnace. Uncombined silicon is removed from the cooled mass

<sup>1</sup> Colson, *Compt. rend.*, 1882, 94, 1316, 1526.

<sup>2</sup> Schutzenberger and Colson, *Compt. rend.*, 1881, 92, 1508, 1892, 114, 1087; Colson, *Bull. Soc. chim.*, 1882, [11], 38, 56.

<sup>3</sup> See *J. Soc. Chem. Ind.*, 1903, 22, 743.

<sup>4</sup> Moissan and Stock, *Compt. rend.*, 1900, 131, 139, *Ber.*, 1900, 33, 2125.

by treatment with a cold mixture of nitric and hydrofluoric acids, and the crystals are further purified by heating them with moist potash for half an hour, washing with nitric acid and hot water, and drying at  $180^{\circ}\text{C}$ .

Each compound may be separated from the mixture by suitable treatment. Boiling nitric acid oxidises the hexaboride, leaving the triboride in black, rhombic plates, of density 2.52, whilst fused anhydrous potash decomposes the triboride and leaves the hexaboride in black, opaque crystals of density 2.17, which are intermediate in hardness between ruby and diamond.

Both borides are good conductors of electricity; fluorine acts vigorously upon them, and chlorine at a red heat; they are stable when heated in the air, but must not be heated in platinum, with which the silicon would combine; concentrated sulphuric acid attacks them slowly at  $330^{\circ}\text{C}$ .

#### DETECTION AND ESTIMATION OF SILICON

The silicon present in a compound of this element is invariably detected and estimated in the form of silica, which is identified by the microcosmic or sodium carbonate bead test. In the former test the silica floats uncombined with the sodium metaphosphate in the clear bead of this substance formed by fusing microcosmic salt; in the latter test silica, by forming a glass, renders transparent the otherwise crystalline and opaque bead of sodium carbonate. The silica may be obtained, sometimes by hydrolysing the compound with water, by fusing it with a mixture of sodium and potassium carbonates and decomposing the resulting silicates with hydrochloric acid, or else by heating it with concentrated sulphuric acid. This latter method is useful for estimating the silicon in an organic compound; the acid burns up all the carbon and leaves a residue of pure silica.

## CHAPTER IV

### TITANIUM AND ITS COMPOUNDS

#### TITANIUM

Symbol, Ti. Atomic weight, 48.1 (O = 16)

**Occurrence.**—Titanium occurs in the crust of the earth in the form of its dioxide,  $\text{TiO}_2$ , which, like silica, is either in the free state or combined with metallic oxides, forming titanates.

Impure titanium dioxide is found in three distinct crystalline forms as *rutile*, *brookite*, and *anatase*; *ilmenite* or titanite iron ore is  $\text{FeTiO}_3$ ; and besides these there are *perovskite*,  $(\text{Ca}, \text{Fe}^{++})\text{TiO}_3$ , *titanite* or *sphen*,  $\text{CaTiSiO}_5$ , *schorlomite*,  $\text{Ca}(\text{Ti}, \text{Fe})\text{SiO}_5$ , and *leilhaute*,  $\text{CaY}(\text{Ti}, \text{Al}, \text{Fe})\text{SiO}_5$ .

Titanium is also widely diffused through many other minerals and rocks. Some iron ores contain this element, which appears in the blast-furnace, after the smelting of these ores, as the cyano-nitride. Titanium is also found in basalt, trap, mica, and other igneous rocks, in sand, clays, soils, and mineral waters. Ninety soils, collected from different parts of the world, contained an average of 0.57 per cent.  $\text{TiO}_2$ .<sup>1</sup> Igneous rocks contain an average of 0.74 per cent. of  $\text{TiO}_2$ , shales 0.65 per cent., sandstones 0.25 per cent., limestones 0.06 per cent., the whole lithosphere containing 0.73 per cent. of this oxide; whilst the element titanium follows oxygen, silicon, aluminium, iron, calcium, sodium, magnesium, potassium, hydrogen in relative abundance in the crust of the earth, and is followed by chlorine, carbon, phosphorus, sulphur, etc.<sup>2</sup> The wide diffusion of titanium in the soil accounts for its passing into the tissues of plants and animals. The ashes of all plants contain it; in the ash of oak, *e.g.*, Wait<sup>3</sup> found 0.31 per cent.  $\text{TiO}_2$ ; also it is present in the flesh and bone of animals, including man; and Baskerville<sup>4</sup> found ox bone to contain 0.0195 per cent.  $\text{TiO}_2$ . Titanium has also been detected in some meteorites, in the sun,<sup>5</sup> and in many stars.<sup>6</sup>

**History.**—In the year 1789 the Rev. William Gregor<sup>7</sup> discovered that a mineral, named *ilmenite*, or *menachante* from the part of Cornwall in which it occurs, contained a hitherto unknown metal. A few years later Klaproth<sup>8</sup> discovered titanium in *rutile*, and showed that this was also the element present in ilmenite. Other titanium minerals

<sup>1</sup> Duddington, *Chem. News*, 1892, 65, 65; 1897, 76, 221

<sup>2</sup> See this series, vol. i, 2nd edition, p. 8

<sup>3</sup> Wait, *J. Amer. Chem. Soc.*, 1896, 18, 402

<sup>4</sup> Baskerville, *J. Amer. Chem. Soc.*, 1899, 21, 1099

<sup>5</sup> Cornu, *Compt. rend.*, 1878, 86, 101, 983; Lockyer and Baxandall, *Proc. Roy. Soc.* 1905, 74, 255; Deslandres, *Compt. rend.*, 1905, 141, 409

<sup>6</sup> Fowler, *Proc. Roy. Soc.*, 1904, 73, A, 219

<sup>7</sup> Gregor, *Crell. Annalen*, 1791, [1], 40, 103

<sup>8</sup> Klaproth, *Researches* (1797), i, 233, 245, ii, 222, 226, iv, 153

were examined by Lampadius,<sup>1</sup> Lowitz,<sup>2</sup> and Vauquelin<sup>3</sup>, but Rose<sup>4</sup> first obtained pure titanium dioxide in 1821. Early attempts were made to prepare metallic titanium by reducing the oxide with carbon; and the product was mistaken for the element on account of its metallic appearance until Wohler, in 1819, proved it to be titanium cyanonitride. So difficult is the preparation of metallic titanium, that it is doubtful if the element has even yet been obtained in the pure state.

**Preparation of Metallic Titanium.** Titanium has been prepared in a more or less pure form in many different ways. The methods employed have included (i) the reduction of halogen compounds by metals or hydrogen, (ii) the reduction of titanium dioxide by carbon, silicon, or metals, (iii) the electrolysis of the oxide or other compound.

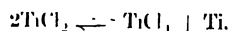
Berzelius<sup>5</sup> and Wohler<sup>6</sup> reduced potassium titan-fluoride,  $K_2TiF_6$ , by heating it with sodium or potassium after the manner of the preparation of silicon.



whilst Wohler and Deville<sup>7</sup> passed the vapour of sodium in a stream of hydrogen over the heated titan-fluoride.

Ebelmen<sup>8</sup> reduced titanium tetrachloride,  $TiCl_4$ , with hydrogen, whilst Deville<sup>9</sup> was the first to reduce this compound with sodium, a reaction which Nilson and Pettersson<sup>10</sup> subsequently carried out in a wrought-iron bomb, and so obtained a product containing 91 per cent. titanium.

Titanium was obtained by Stahler and Bachman by the ignition of the dichloride in a current of hydrogen at  $1100^\circ C$ .<sup>11</sup>



When titanium dioxide is reduced with sodium only the lower oxide results, if magnesium is employed the lower oxide is mixed with hydride,<sup>12</sup> whilst aluminium, employed as in the Goldschmidt reaction, yields only an alloy.<sup>13</sup>

When titanium dioxide is reduced with silicon the product always contains this element; and reduction with carbon always yields a product containing, besides carbon, nitrogen absorbed from the air. Moissan<sup>14</sup> has employed this reaction in the electric furnace, however, and has obtained a nearly pure form of titanium by the following method: Artificial titanic oxide is intimately mixed with carbon, then dried and compressed in a cylindrical carbon crucible, which is heated in the electric furnace above the decomposition temperature of the nitride. Fused titanium is thus obtained, above a yellow layer of nitride, below

<sup>1</sup> Lampadius, *Crill Annalen*, 1796, [1], 259.

<sup>2</sup> Lowitz, *Crill Annalen*, 1799, [1], 183.

<sup>3</sup> Vauquelin, *J. Physique*, 66, 345.

<sup>4</sup> Rose, *Gilb Annalen*, 1821, 73, 67, 129.

<sup>5</sup> Berzelius, *Ann. Physik*, 1823, 4, 3.

<sup>6</sup> Wohler, *Annalen*, 1819, 73, 34, 1819, 74, 212, *Jahresber.*, 1819, 266.

<sup>7</sup> Wohler and Deville, *Annalen*, 1857, 103, 230.

<sup>8</sup> Ebelmen, *J. prakt. Chem.*, 1846, 42, 70.

<sup>9</sup> Deville, *Compt. rend.*, 1855, 40, 1034.

<sup>10</sup> Nilson and Pettersson, *Zeit. physikal. Chem.*, 1887, 1, 28; see also Hunter, *J. Amer. Chem. Soc.*, 1910, 32, 330, and Weiss and Karsel, *Zeitsch. anorg. Chem.*, 1910, 65, 345.

<sup>11</sup> Stahler and Bachman, *Ber.*, 1911, 44, 2906.

<sup>12</sup> Winkler, *Ber.*, 1890, 23, 2661.

<sup>13</sup> Stavenhagen and Schuchard, *Ber.*, 1902, 35, 909.

<sup>14</sup> Moissan, *Compt. rend.*, 1895, 120, 290.

which is the crystalline oxide. The titanium still contains a variable proportion of carbon, which is removed by heating it again as before with more oxide. Thus the metal is obtained free from silicon and nitrogen, but containing about 2 per cent. of carbon. Finally, the metal may be distilled in the electric furnace at a temperature of about 3500° C. under atmospheric pressure and condensed in minute crystals.<sup>1</sup> Wedekind has obtained titanium in a high state of purity by heating titanate oxide with calcium shavings in an evacuated iron vessel.<sup>2</sup>

Borchers and Huppertz have prepared titanium by the reduction of its oxide by electrolytic calcium, the oxide being melted in a bath of fused calcium chloride undergoing electrolysis; and it is claimed that the product is quite free from nitrogen and carbon.<sup>4</sup> Kongsberger and Schilling<sup>4</sup> have prepared titanium containing only a trace of iron and silicon by the electrolysis of rutile with carbon electrodes.

**Physical Properties.**—The impure titanium prepared by Berzelius and Wohler was a grey powder; the almost pure metal obtained in fused masses by Moissan's method is brittle, breaking with a white fracture, and sufficiently friable to be powdered in an agate mortar. It is nevertheless hard enough to scratch quartz and steel. Crystalline titanium is isomorphous with zirconium and silicon; Moissan's metal has a density of 4.87.<sup>5</sup> The specific heat of titanium is variable, and the atomic heat of the impure metal examined by Nilson and Pettersson<sup>6</sup> exceeded 6.4 at high temperatures, as the following figures show:

Temperature Interval ° C.	Specific Heat	Atomic Heat
0 to 100	0.1125	5.40
0 „ 211	0.1288	6.18
0 „ 301.5	0.1485	7.13
0 „ 110	0.1620	7.77

The melting-point of titanium is given as 1795° C.<sup>7</sup> The spark spectra obtainable from solutions of titanium compounds have been studied by Pollok<sup>8</sup>; and the long-waved portion of the spectrum has been mapped by Fiebig.<sup>9</sup>

The most intense lines in the spectrum of titanium are as follow<sup>10</sup>:

Acrc : 3948.87, 3989.94, 3998.80, 4306.09, 4533.40, 4536.16, 4981.93, 4991.24, 4999.68, 5007.35, 5014.39, 5193.12, 5210.59.

<sup>1</sup> Moissan, *Compt. rend.*, 1906, 142, 673

<sup>2</sup> Wedekind, *Annalen*, 1913, 395, 149

<sup>3</sup> Huppertz, *Metallurgie*, 1904, 302 et seq.

<sup>4</sup> Kongsberger and Schilling, *Physikal. Zeitsch.*, 1908, 9, 347

<sup>5</sup> See also Weiss and Kaiser, *Zeitsch. anorg. Chem.*, 1910, 65, 315, and Hunter *J. Amer. Chem. Soc.*, 1910, 32, 330

<sup>6</sup> Nilson and Pettersson, *Zeitsch. physikal. Chem.*, 1887, 1, 28

<sup>7</sup> Burgess and Waltenberg, *J. Washington Acad. Sci.*, 1913, 3, 371; *Zeitsch. anorg. Chem.*, 1913, 88, 361.

<sup>8</sup> Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1909, 11, 331

<sup>9</sup> Fiebig, *Zeitsch. wiss. Photochem.*, 1910, 8, 73

<sup>10</sup> Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911)

Spark : 2516·10, 3361·10,\* 3372·92,\* 3383·87, 3505·10, 3510·90, 3685·37,\* 3759·16,\* 3900·81, 3913·72, 4163·90, 4395·20, 4549·90, 4572·27.

The four lines asterisked, together with 3761·5 and 3319·2, constitute the most *persistent*, i.e. the ultimate spark lines of titanium.<sup>1</sup>

**Chemical Properties.**—Titanium is stable in the air, very little oxidation taking place even at 100–120° C.; but it burns brilliantly in oxygen at 610° C., forming titanic oxide, and in nitrogen at 800° C., producing the nitride TiN. This is the only known case of vigorous combustion in nitrogen gas. By combustion in air a mixture of oxide and nitride results; nitride is also formed when the metal is heated in ammonia gas. The heat of combustion of the metal is 21·432 calories per equivalent.<sup>2</sup> Chlorine combines with titanium at 350° C., forming the tetrachloride TiCl<sub>4</sub>; bromine forms the tetrabromide TiBr<sub>4</sub> at 360° C., iodine forms the corresponding iodide TiI<sub>4</sub> at a still higher temperature. Carbon, silicon, and boron combine with molten titanium in the electric furnace; the crystallised borides and silicides are as hard as diamond. Alloys of titanium with copper, tin, iron, aluminium, chromium, cobalt, molybdenum, and tungsten are known. Pyrophoric titanium decomposes steam at 700–800° C. Titanium dissolves slowly in cold, dilute sulphuric acid, and in hot concentrated hydrochloric acid, with evolution of hydrogen, and formation, according to Moissan, of violet solutions of salts of the sesqui-oxide. Nitric acid and aqua regia form titanic acid.

“The whole of the properties of titanium bring it clearly near to the metalloids and more especially to silicon” (Moissan<sup>3</sup>).

#### ATOMIC WEIGHT OF TITANIUM

The earliest accepted values for the atomic weight of titanium were inaccurate on account of imperfect analytical methods. Thus Dalton, in 1808, gave the value Ti = 40 (O = 7), whilst Berzelius in 1813 suggested the number 1801·0 (O = 100) or 288·16 (O = 16). That the atomic weight of titanium must be of the order of 48 is evident from the following considerations:

(1) The specific heat of the metal between 0° C. and 110° C. ranges from 0·112 to 0·162. Assuming a mean atomic heat of 6·4, according to the law of Dulong and Petit,<sup>4</sup> the atomic weight of titanium must lie between 57 and 40.

(2) Rutile is isomorphous with cassiterite (SnO<sub>2</sub>); and fluoritanates are isomorphous with fluosilicates, M<sub>2</sub>SiF<sub>6</sub>, fluozirconates, M<sub>2</sub>ZrF<sub>6</sub>, and fluostannates, M<sub>2</sub>SnF<sub>6</sub>. From Mitscherlich's Law of Isomorphism<sup>5</sup> it follows that the formula for rutile is TiO<sub>2</sub>, whilst the general formula for fluoritanates is M<sub>2</sub>TiF<sub>6</sub>. Now analysis shows that each of these gram-molecules contains approximately 48 grams of titanium. This latter weight, therefore, is approximately the atomic weight of the element.

(3) There is a space in the fourth group of the Periodic Table (see Frontispiece) for an element of atomic weight lying between 44 and 51.

<sup>1</sup> Pollok, *Sci. Proc. Roy. Dubl. Soc.*, 1909, **11**, 331.

<sup>2</sup> Weiss and Kaiser, *Zeitsch. anorg. Chem.*, 1910, **65**, 345.

<sup>3</sup> Moissan, *The Electric Furnace*, Eng. edn. (Arnold, 1901), p. 181.

<sup>4</sup> See this series, vol. 1, p. 94.

<sup>5</sup> See this series, vol. 1, p. 71.



The chemical and physical properties of titanium indicate that this is the element required satisfactorily to fill the gap. Judging by comparison of the differences between the atomic weights of other adjacent elements in the table, the atomic weight of titanium should approximate to 48.

The analytical investigations on which the atomic weight of titanium is based fall into two categories: (i) the work of Berzelius, H. Rose,<sup>1</sup> Mosander,<sup>2</sup> Pierre,<sup>3</sup> and Demoly<sup>4</sup> from 1813 to 1849; (ii) the work of Thorpe,<sup>5</sup> 1883-1885.

Except for the early work of Berzelius, and that of H. Rose in 1823, who prepared the disulphide  $\text{TiS}_2$ , and converted it into the dioxide  $\text{TiO}_2$ , the processes adopted have consisted in hydrolysing the pure tetrachloride or tetrabromide with water or alkali, and estimating the titanic oxide and the hydrochloric or hydrobromic acid produced. The titanic oxide was estimated by Thorpe by decomposing the tetrachloride with water in a platinum or porcelain dish, according to the reaction



evaporating with ammonia, and then igniting and weighing the residue. The halogen hydracid was estimated by hydrolysing the titanium halide, allowing the solution to stand until it was clear, then either precipitating nearly all the halogen with a known weight of pure silver dissolved in nitric acid, and finishing the estimation by titrating with centnormal silver solution, or by adding excess of silver solution and weighing the silver halide precipitated.

The results of Thorpe alone are accepted in computing the atomic weight of titanium. They are as follows:

Ratio	Atomic Weight of Titanium <sup>a</sup>
$\text{TiCl}_4 : \text{Ag} \quad 0.13997 : 1$	48.03
$\text{TiCl}_4 : \text{AgCl} \quad 0.33119 : 1$	48.06
$\text{TiCl}_4 : \text{TiO}_2 \quad 2.3712 : 1$	48.09
$\text{TiBr}_4 : \text{Ag} \quad 0.85234 : 1$	48.14
$\text{TiBr}_4 : \text{AgBr} \quad 0.48965 : 1$	48.16
$\text{TiBr}_4 : \text{TiO}_2 \quad 4.5931 : 1$	48.06
Mean value	48.09

The mean value adopted by the International Committee on Atomic Weights for 1917 is **48.1**.

<sup>1</sup> Rose, *Gilbert's Annalen*, 1823, 73, 141, *Pogg Annalen*, 1829, 15, 145.

<sup>2</sup> Mosander, *Pogg Annalen*, 1830, 19, 212.

<sup>3</sup> Pierre, *Ann Chim Phys*, 1847, [iii], 20, 257.

<sup>4</sup> Demoly, *Annalen*, 1849, 72, 213.

<sup>5</sup> Thorpe, *Trans. Chem Soc.*, 1885, 47, 108.

<sup>a</sup> These are not the figures given by Thorpe, but have been recalculated from the values of Thorpe's ratios, using the modern atomic values, O = 16, Cl = 35.457; Br = 79.916 and Ag = 107.880.

## COMPOUNDS OF TITANIUM

The relation of titanium to other elements of the fourth and other groups has been fully discussed in the introductory chapter. It will be useful to set forth here the types of compound formed by this element, since these are varied, in accordance with the fact that titanium may show bi-, tri- or quadri-valency.

	II	III	IV
Halides	TiCl <sub>3</sub>	TiCl <sub>3</sub>	TiF <sub>4</sub> , K <sub>2</sub> TiF <sub>6</sub> , TiCl <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> TiCl <sub>6</sub> , TiCl(OH) <sub>2</sub> , Ti(OH) <sub>2</sub> , TiCl(OH) <sub>3</sub> , Ti <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O
Oxides and hydroxides	TiO <sub>2</sub> , Ti(OH) <sub>2</sub> , TiO <sub>3</sub>	Ti <sub>2</sub> O <sub>3</sub> , Ti(OH) <sub>3</sub> ·H <sub>2</sub> O	TiO <sub>2</sub> , Ti(OH) <sub>4</sub> , Ti <sub>2</sub> O <sub>3</sub> , Ti(OH) <sub>3</sub> , Ti <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O, Ti <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O, Titanates
Sulphides	TiS <sub>2</sub>	TiS <sub>2</sub>	TiS <sub>2</sub>
Sulphates	—	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , and double salts, not mg an alum	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , basic and double salts
Nitrides	—	TiN	Ti <sub>3</sub> N <sub>4</sub>
Superoxide	TiO <sub>2</sub> , Ti <sub>2</sub> O <sub>3</sub> or Ti(OH) <sub>3</sub> ·H <sub>2</sub> O, or (NH <sub>4</sub> ) <sub>2</sub> O <sub>2</sub> ·TiO <sub>2</sub> ·H <sub>2</sub> O <sub>2</sub>	—	—
Perfluorates	—	—	—

## TITANIUM AND FLUORINE

**The Fluorides.** Titanium difluoride is unknown, the tri- and tetrafluorides are well-known substances which give rise to corresponding complex salts.

**Titanium Trifluoride, TiF<sub>3</sub>.** When titanium is dissolved in hydrofluoric acid the trifluoride alone results, but the trifluoride is formed as an insoluble violet powder when potassium titanfluoride, K<sub>2</sub>TiF<sub>6</sub>, is ignited in a current of hydrogen,<sup>1</sup> or when the same substance is reduced in solution with zinc and hydrochloric acid,<sup>2</sup> or by sodium amalgam.<sup>3</sup> The complex salts (NH<sub>4</sub>)<sub>2</sub>TiF<sub>5</sub> and (NH<sub>4</sub>)<sub>3</sub>TiF<sub>6</sub> have been obtained<sup>4</sup>; and the latter appears to be isomorphous with (NH<sub>4</sub>)<sub>3</sub>CrF<sub>6</sub>, (NH<sub>4</sub>)<sub>3</sub>VF<sub>6</sub> and (NH<sub>4</sub>)<sub>3</sub>FeF<sub>6</sub>.

**Titanium Tetrafluoride, TiF<sub>4</sub>.** Impure titanium tetrafluoride is formed when magnesium titanfluoride, Mg<sub>2</sub>TiF<sub>6</sub>,<sup>5</sup> or the corresponding barium salt, BaTiF<sub>6</sub>,<sup>6</sup> is decomposed by strong ignition; but it is best prepared by one of the three following methods: (i) the action of fluorine on titanium, (ii) the action of anhydrous hydrogen fluoride

<sup>1</sup> Weber, *J. prakt. Chem.*, 1863, 90, 212

<sup>2</sup> Rammelsberg, *Sitzungsber. K. Akad. Wiss. Berlin*, 1871, 490

<sup>3</sup> Von der Pfordten, *Annalen*, 1886-7, 234, 257, 257, 261

<sup>4</sup> Piccini, *Chem. Zentr.*, 1896, 1, 470, Petersen, *J. prakt. Chem.*, 1889, [n], 40, 44.

<sup>5</sup> Margnac, *Ann. Chim. Phys.*, 1860, [m], 60, 257

<sup>6</sup> Emich, *Monatsh.*, 1904, 25, 907

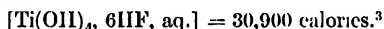
on titanium, (iii) the action of anhydrous hydrogen fluoride on titanium tetrachloride at 100°–120° C.; for, owing to the high volatility of hydrogen chloride compared with hydrogen fluoride, the reaction<sup>1</sup>



proceeds in one direction only.

Titanium tetrafluoride<sup>2</sup> is a colourless mass having a density 2.798 at 20.5° C. It boils at 284° C. and at 144° C. has a vapour density of 64.5 (theory = 62.05). It is noteworthy that the boiling-point of the fluoride is above that of the tetrachloride,  $\text{TiCl}_4$  (136° C.); this probably indicates that the former is polymerised near its boiling-point. This difference between the tetrafluoride and tetrachloride is in marked contrast with that between the silicon halides,  $\text{SiF}_4$  and  $\text{SiCl}_4$ , and the corresponding halides of other non-metals and metalloids, and relates titanium to the metals rather than the metalloids. The same nature of the fluoride is further shown by the fact that it is hygroscopic, and forms a clear solution in water, which deposits the hydrate  $\text{TiF}_4 \cdot 2\text{H}_2\text{O}$  on evaporation. With alcohol the compound  $\text{TiF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  is formed, and with ammonia the compound  $\text{TiF}_4 \cdot 2\text{NH}_3$ ; but, singularly, it does not combine directly with hydrogen fluoride, although the salts  $\text{M}_2\text{TiF}_6$  are so well known. Roasting with sulphuric acid converts titanium tetrafluoride into titanic oxide.

**Hydrofluotitanic Acid and the Titanifluorides.**—Hydrofluotitanic acid,  $\text{H}_2\text{TiF}_6$ , is not known in the pure state, but is formed in solution when titanic oxide is dissolved in aqueous hydrofluoric acid, the heat of solution being:



As a result of this reaction the solution increases in electric conductivity, since hydrofluotitanic acid is a much stronger acid than hydrofluoric acid.

Numerous titanifluorides are known which generally correspond to the type  $\text{M}'_2\text{TiF}_6$  and are isomorphous with the silic-, zircon-, and stann-fluorides.

Titanifluorides differ from silicfluorides in their behaviour when heated with concentrated sulphuric acid; for, owing to the comparative non-volatility of titanium tetrafluoride this latter compound is not vaporised, as is silicon tetrafluoride from a silicfluoride under similar conditions, but the titanium is converted quantitatively into titanic oxide. On this account titanium tetrafluoride cannot be prepared by heating calcium fluoride and titanic oxide with sulphuric acid.

The titanifluorides are formed by the union of their component fluorides,<sup>4</sup> and, like various other complex salts, are characterised by sparing solubility in water.

**Potassium Titanifluoride**,  $\text{K}_2\text{TiF}_6$ , is obtained crystallised in lustrous leaflets when potassium hydrogen fluoride is added to a solution of titanic oxide in concentrated hydrofluoric acid, and it may be recrystallised from hydrofluoric acid.<sup>5</sup> The hydrated salt,  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ , separates

<sup>1</sup> Ruff, Plato, and Graf, *Ber.*, 1904, 37, 673.

<sup>2</sup> Ruff and Ipsen, *Ber.*, 1903, 36, 1777.

<sup>3</sup> Thomsen, *Pogg. Annalen*, 1870, 139, 212.

<sup>4</sup> Berzelius, *Ann. Physik*, 1825, 4, 3; Maignac, *Ann. Chim. Phys.*, 1860, [iii], 60, 257.

<sup>5</sup> Marchetti, *Zeitsch. anorg. Chem.*, 1895, 10, 66.

in shining scales when potash is added to an aqueous solution of hydrofluotitanic acid. It loses its water at 100° C., and melts at a white heat without decomposition.

The solubility of potassium titanifluoride in water is as follows<sup>1</sup>:

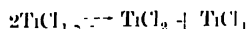
Temperature " C. . . . .	0°	3"	6'	10	14	20'
Grams of K <sub>2</sub> TiF <sub>6</sub> in 100						
grams H <sub>2</sub> O . . . . .	0.55	0.67	0.77	0.91	1.04	1.28

**Sodium Titanifluoride**, Na<sub>2</sub>TiF<sub>6</sub>, is prepared similarly to the potassium salt, than which it is more soluble in water (*c/* K<sub>2</sub>PtCl<sub>6</sub> : Na<sub>2</sub>PtCl<sub>6</sub>). Na<sub>3</sub>HTiF<sub>6</sub> also is known. Two ammonium salts are known—(NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> and (NH<sub>4</sub>)<sub>3</sub>TiF<sub>7</sub>. Numerous other titanifluorides have been described,<sup>2</sup> including those of all the alkali metals, magnesium, the alkaline earth metals, copper, zinc, ferrous iron, nickel, cobalt, manganese, and cadmium.

## TITANIUM AND CHLORINE

**Chlorides.**—Titanium forms di-, tri- and tetrachlorides, and the latter compound gives rise to complex and basic salts.

**Titanium Dichloride**, TiCl<sub>2</sub>, was first prepared by Friedel and Guérin,<sup>3</sup> who heated the trichloride to a red heat in a current of hydrogen, thus decomposing it into the tetrachloride, which distilled, and the dichloride, which remained behind, von der Pfordten<sup>4</sup> however, reduced the cold tetrachloride with sodium amalgam or hydrogen sulphide, and distilled off the unchanged tetrachloride in a current of carbon dioxide. Stahler and Bachran<sup>5</sup> have obtained the dichloride nearly pure by heating the trichloride at 660°–700° C. in an atmosphere of hydrogen:



The dichloride remains after the volatilisation of the tetrachloride as a deep black powder which begins to sublime at 300° C. in a vacuum.

The properties of the dichloride have been variously described. According to Friedel and Guérin it is a brown powder which decomposes water and alcohol, evolving hydrogen and forming a yellow solution; while, according to von der Pfordten, it dissolves unchanged in these solvents, forming yellow solutions which gradually oxidise in the air. It is insoluble in non-hydroxylic solvents—a fact which suggests its saline character; it burns in the air, evolving titanium tetrachloride vapour and forming titanic oxide; it combines with bromine to form a chlorobromide. A satisfactory test for bivalent titanium is the formation of a violet colour, due to TiCl<sub>2</sub>, when it is mixed with a hydrochloric acid solution of titanium tetrachloride.<sup>5</sup>

**Titanium Trichloride**, TiCl<sub>3</sub>.—Titanium trichloride was first obtained in the anhydrous state by Ebelmen,<sup>6</sup> who passed a mixture of the vapour of the tetrachloride and hydrogen through a red-hot tube and found the trichloride deposited in the cold part of the tube. Large

<sup>1</sup> Marignac, *Ann. Chim. Phys.*, 1866, [iv], 8, 65.

<sup>2</sup> Emich, *Monatsh.*, 1904, 25, 907. Engelskirchen, *Dissertation, Technische Hochschule, Berlin*, 1903; Weber, *J. prakt. Chem.*, 1864, 90, 212; Gosner, *Ber.*, 1907, 40, 2372.

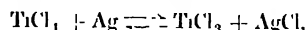
<sup>3</sup> Friedel and Guérin, *Ann. Chim. Phys.*, 1876, [vi], 7, 24.

<sup>4</sup> Von der Pfordten, *Annalen*, 1886, 234, 257; 1887, 237, 201.

<sup>5</sup> Stahler and Bachran, *Ber.*, 1911, 44, 2906.

<sup>6</sup> Ebelmen, *Jahresber.*, 1847–8, p. 402.

quantities of titanium trichloride have been prepared by Goerges and Stahler<sup>1</sup> according to this reaction, by the employment of a porcelain tube heated electrically by means of a wire spiral within it and cooled externally by water. The reaction began above 600° C., at 785° C. the percentage decomposition was 21.7, at 1200° C. it was 94.3. The trichloride is also formed when the tetrachloride is heated in a sealed tube with reduced silver<sup>2</sup> at 180°-200° C.:



when the same substance is heated with mercury,<sup>3</sup> and when electric sparks<sup>4</sup> are passed through a mixture of the vaporised tetrachloride and hydrogen. Titanium trichloride is produced in solution by reducing a hydrochloric acid solution of the tetrachloride with zinc, or electrolytically.<sup>5</sup> The anhydrous trichloride forms dark violet scales which are not volatile, but when heated to 440° C.<sup>6</sup> decompose into the tetrachloride which is vaporised, and the dichloride which remains behind. By passing the silent electric discharge through a mixture of titanium tetrachloride vapour and hydrogen, Bock and Moser<sup>7</sup> obtained a brown substance, which appeared to be a labile, allotropic form of the trichloride, since it changed into the ordinary form of the latter when heated in a vacuum to 150°-200° C. The reaction is not reversible, the brown and violet trichlorides being monotropic modifications. When the trichloride is heated in air the tetrachloride vaporises, and the residue then consists of the dioxide. The trichloride is deliquescent, and forms a reddish violet solution with water, whilst its alcoholic solution is green.

From hydrochloric acid solution titanium trichloride separates in violet crystals of the hexahydrate  $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ ; it is thus obtained by the electrolytic reduction<sup>8</sup> of the tetrachloride. When a concentrated aqueous solution of the violet hydrate is covered with a layer of ether, and saturated with hydrogen chloride while it is kept cool, an unstable green hydrated form,<sup>9</sup>  $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ , separates in crystals, which are reconverted into the violet form when the excess of hydrogen chloride is washed out with ether. Thus titanium trichloride resembles the trichlorides of chromium and vanadium in existing in two forms.

When hydrogen chloride is passed through concentrated aqueous solutions of titanium trichloride with the corresponding alkali chlorides, the double salts,  $\text{TiCl}_3 \cdot 2\text{RbCl} \cdot \text{H}_2\text{O}$  and  $\text{TiCl}_3 \cdot 2\text{CsCl} \cdot \text{H}_2\text{O}$ , separate.<sup>10</sup> They are green, but yield violet solutions owing to dissociation into their component salts.

It was observed by Ebelmen that titanium trichloride is a powerful reducing agent, as shown by its action on salts of copper and iron. The capabilities of this compound as a reducing agent have been exhaustively

<sup>1</sup> Goerges and Stahler, *Ber.*, 1900, 42, 3200.

<sup>2</sup> Friedel and Guérin, *Compt. rend.*, 1875, 81, 889; 1876, 82, 509, 972.

<sup>3</sup> Thorpe, *Chem. News*, 1885, 51, 260.

<sup>4</sup> Emich, *Ber.*, 1895, 28, 1585.

<sup>5</sup> Polidori, *Zeitsch. anorg. Chem.*, 1899, 19, 306; Stahler, *Ber.*, 1901, 37, 4405.

<sup>6</sup> Goerges and Stahler, *loc. cit.*

<sup>7</sup> Moser, *Monatsh.*, 1912, 33, 1407; 1913, 34, 1825.

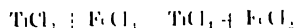
<sup>8</sup> Spence and Sons, *D.R.P.*, 154,542.

<sup>9</sup> Stahler and Wirthwein, *Ber.*, 1905, 38, 2619.

<sup>10</sup> Stahler, *Ber.*, 1904, 37, 4405.

studied by Knecht and Hibbert,<sup>1</sup> who have devised a number of volumetric processes depending on its use. The reagent is prepared by dissolving the metal in hydrochloric acid, or by metallic or electrolytic reduction of the tetrachloride; it may now be purchased in 20 per cent aqueous solution. When a dilute aqueous solution of titanium trichloride, which is violet, is exposed to the air its colour fades, and titanic hydroxide is gradually precipitated; the presence of sufficient hydrochloric acid, however, prevents this precipitation. Titanium trichloride is a more powerful reducing agent than stannous chloride, and the following reductions are effected by this substance: concentrated nitric acid, with violent action, to nitrous fumes and ammonia; dilute nitric acid, in presence of hydrochloric acid, to a stage intermediate between nitric and nitrous oxides; chlorates and perchlorates to chlorides; hydrogen peroxide to water; persulphates to sulphates; sulphurous acid to hyposulphurous acid ( $\text{H}_2\text{S}_2\text{O}_3$ ), which is thus conveniently prepared; ferric salts to ferrous salts; cupric salts to cuprous salts and copper; mercuric chloride to mercurous chloride, only on boiling; chromic and permanganic acids to chromic and manganous salts. The use of titanium trichloride in qualitative analysis, on account of its characteristic reactions, is recommended by Monnier.<sup>2</sup> Titanium trichloride reacts with a gold solution like stannous chloride, producing colloidal gold, analogous to purple of Cassius. This reaction will detect one part of gold in twenty million parts of water.<sup>3</sup> Many organic substances also undergo interesting reductions in presence of titanium trichloride.

For volumetric analysis<sup>4</sup> the commercial solution of titanium trichloride is diluted twenty times and stored under hydrogen. It is standardised by means of ferric solution with which it reacts quantitatively thus:



The end of the reaction is shown by sulphocyanide or methylene-blue<sup>5</sup> solution used as an external indicator. Titanium trichloride solution may be employed for estimating not only iron but also copper, tin, chromium, hydrogen peroxide, chlorates, perchlorates, nitrates, hydroxylamine, hyposulphites (hydrosulphites), and numerous organic compounds, including dye-stuffs.<sup>6</sup>

**Titanium Tetrachloride** (*Titanic Chloride*),  $\text{TiCl}_4$ . Titanium and chlorine combine when heated together to  $350^\circ\text{C}$ . forming titanium tetrachloride. In place of the pure metal that containing carbon,<sup>7</sup> or the carbide,<sup>8</sup> may be employed. This chloride is also conveniently prepared, like non-metallic chlorides, by passing chlorine over a heated mixture of titanic oxide and carbon, as well as by leading the vapour of carbon tetrachloride or chloroform<sup>9</sup> over the heated dioxide. Ferro-

<sup>1</sup> Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis* (Langmans, 1910).

<sup>2</sup> Monnier, *Ann. Chim. Anal.*, 1915, 20, 1.

<sup>3</sup> Stahler and Bachman, *Ber.*, 1911, 44, 2906.

<sup>4</sup> Knecht and Hibbert, *Ber.*, 1903, 36, 1519.

<sup>5</sup> Knecht and Hibbert, *Ber.*, 1909, 43, 3155.

<sup>6</sup> Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis* (Langmans, 1910).

<sup>7</sup> Wohler, *Annalen*, 1819, 73, 31. 1850, 74, 242.

<sup>8</sup> Moissan, *Compt. rend.*, 1895, 120, 290; Stahler, *Ber.*, 1904, 37, 4405, 1905, 38, 2619.

<sup>9</sup> Renz, *Ber.*, 1906, 39, 249.

titanium may also be used as a source of the tetrachloride.<sup>1</sup> Most of the iron is first removed by hydrochloric acid, and the residue is heated in a porcelain tube through which chlorine is passed. Ferric chloride condenses in the cooler parts of the tube, and titanic chloride is obtained by further cooling and then fractionated. In another process rutile<sup>2</sup> is reduced by aluminium according to the Goldschmidt reaction, and the product heated in a current of chlorine; the crude titanic chloride thus obtained needs to be separated by fractional distillation from silicon tetrachloride, derived from the silica of the rutile.

Titanium tetrachloride is a colourless, mobile liquid of density 1.7604 at 0° C and 1.5222 at its boiling-point<sup>3</sup>. It boils at 136.1° C. under 760 mm. pressure (Thorpe), its critical temperature<sup>4</sup> is 358° C., at low temperature it forms a solid mass which melts<sup>5</sup> at - 23° C. The vapour density was found by Dumas to be 6.836 (air = 1) or 197.4 (O = 16), theory requiring 190 in the latter case.

Titanium tetrachloride has a penetrating smell, and fumes excessively in moist air. With water it forms a series of oxychlorides,  $\text{TiCl(OH)}$ ,  $\text{TiCl}_2(\text{OH})_2$ ,  $\text{TiCl(OH)}_3$ <sup>6</sup>, with excess of water  $\text{Ti(OH)}_4$  is formed; nevertheless titanium tetrachloride dissolves in water with evolution of considerable heat, the hydrochloric acid formed simultaneously with the titanic hydroxide sufficing to redissolve the voluminous precipitate of  $\text{Ti(OH)}_4$  first formed.<sup>7</sup> According to Thomson<sup>8</sup> the heat evolved by the solution of 1 molecule of  $\text{TiCl}_4$  in 1600 molecules of water at 17° C is 57,870 calories. In its behaviour towards water titanium tetrachloride stands between the tetrachlorides of silicon and tin.

Sodium amalgam at ordinary temperature reduces the tetrachloride to dichloride, hydrogen at red heat reduces it to the trichloride.

**Titanium Oxychlorides.** - In addition to the hydroxychlorides mentioned above, several oxychlorides of titanium have been prepared in the dry way; for example, by the interaction of the tetrachloride and the dioxide, and by the action of carbon tetrachloride on  $\text{TiO}_2$ , when a yellow, crystalline oxychloride results. Troost and Hautefeuille<sup>9</sup> obtained a solid of the composition  $\text{Ti}_2\text{O}_3\text{Cl}_2$  by passing a mixture of oxygen and  $\text{TiCl}_4$  vapour through a red-hot tube, and Bourion<sup>10</sup> obtained a yellow liquid, supposed to be an oxychloride, by causing chlorine and sulphur monochloride to interact with ignited  $\text{TiO}_2$ .

**Compounds of Titanic Chloride.** - Titanic chloride forms numerous additive compounds, the chief of which are here enumerated:

*Hydrochlorotitanic Acid,  $\text{H}_2\text{TiCl}_6$ , and its Salts.* Titanic chloride dissolves in concentrated hydrochloric acid, forming a yellow liquid<sup>11</sup> which contains hydrochlorotitanic acid,  $\text{H}_2\text{TiCl}_6$ . Ammonium titanic chloride,  $(\text{NH}_4)_2\text{TiCl}_6 \cdot 2\text{H}_2\text{O}$ , forms in yellow crystals when the theo-

<sup>1</sup> Vigoureux and Arisaut, *Bull. Soc. chim.*, 1907, [iv], 1, 19.

<sup>2</sup> Ellis, *Chem. News*, 1907, 95, 122.

<sup>3</sup> Thorpe, *Proc. Roy. Soc.*, 1876, 24, 283, *Trans. Chem. Soc.*, 1880, 37, 141.

<sup>4</sup> Goldberg, *Ann. Physik. Beibl.*, 1883, 7, 350.

<sup>5</sup> Emich, *Monatsh.*, 1904, 25, 907.

<sup>6</sup> König and von den Pförden, *Ber.*, 1889, 22, 1485.

<sup>7</sup> Kowalewsky, *Zeitsch. anorg. Chem.*, 1900, 25, 139.

<sup>8</sup> Thomson, *Pogg. Annalen*, 1870, 139, 212.

<sup>9</sup> Troost and Hautefeuille, *Compt. rend.*, 1871, 73, 563.

<sup>10</sup> Bourion, *Compt. rend.*, 1907, 145, 62.

<sup>11</sup> Kowalewsky, *Zeitsch. anorg. Chem.*, 1900, 25, 189, Rosenheim and Schütte, *Zeitsch. anorg. Chem.*, 1901, 26, 239.

retical quantity of ammonium chloride is shaken with the hydrochloric acid solution of titanium tetrachloride, pyridine, quinoline, and aniline form similar complex salts.

**Addition Compounds of Titanium Tetrachloride.** Besides hydrochlorotitanic acid and its salts, titanium forms numerous addition products with ammonia and other bases, as well as with various acid chlorides.

With ammonia there are the compounds  $\text{TiCl}_4 \cdot 8\text{NH}_3$  and  $\text{TiCl}_4 \cdot 6\text{NH}_3$ , and perhaps  $\text{TiCl}_4 \cdot (\text{NH}_3)_4$ .

The compound  $\text{TiCl}_4 \cdot 8\text{NH}_3$  is formed as a yellow powder<sup>2</sup> when dry ammonia reacts with titanium tetrachloride suspended in dry ether, and also when the tetrachloride is shaken for twelve hours with liquid ammonia. It is unstable, readily giving up ammonia. The compound  $\text{TiCl}_4 \cdot 6\text{NH}_3$  results when gaseous ammonia reacts with the tetrachloride vapour; it is an amorphous, dark yellow powder which in presence of a little moisture is readily hydrolysed, yielding titanic acid, ammonium chloride, and ammonia. Liquid ammonia reacts with either of these compounds, yielding dark yellow titanamide,  $\text{Ti}(\text{NH}_2)_4$ , and ammonium chloride.

A pyridine compound,<sup>3</sup>  $\text{TiCl}_4 \cdot 6\text{C}_5\text{H}_5\text{N}$ , exists, analogous to the ammonia compound of similar composition, and compounds with acid chlorides, such as  $\text{TiCl}_4 \cdot \text{POCl}_3$ ,  $\text{TiCl}_4 \cdot 2\text{POCl}_3$ ,  $\text{TiCl}_4 \cdot \text{PCl}_5$ ,  $\text{TiCl}_4 \cdot \text{PCl}_6$ , as well as additive compounds with numerous types of organic compounds, are known.

Organic substitution products of titanium tetrachloride have been prepared by Dilthey<sup>4</sup> and his collaborators. For example, acetyl-methylacetone forms the compound  $[\text{Ti}(\text{OCMe} \cdot \text{CMc} \cdot \text{Ac})_2\text{Cl}]_2 \cdot \text{TiCl}_4$  or  $[\text{Ti}(\text{OCMe} \cdot \text{CMc} \cdot \text{Ac})_2]_2 \cdot \text{TiCl}_6$ . Such compounds are called titanonium salts; and there exist corresponding siliconium and boronium compounds.

## BROMIDES OF TITANIUM

Titanium dibromide is unknown, but the tri- and tetra-bromide exist.

**Titanium Tribromide Hexahydrate**,  $\text{TiBr}_3 \cdot 6\text{H}_2\text{O}$ , separates in violet crystals when a solution of the tetrabromide is reduced electrolytically, and the solution is then saturated with hydrogen bromide.<sup>5</sup> It is less stable than the corresponding chloride, and deliquesces in the air forming a brown, fuming liquid.

**Titanium Tetrabromide** (*Titanic Bromide*),  $\text{TiBr}_4$ , is said to be formed when bromine vapour is passed over a red-hot mixture of titanic oxide and carbon,<sup>6</sup> but is prepared by the action of gaseous hydrogen bromide on the heated chloride.<sup>7</sup> It is an amber-colored hygroscopic, crystalline substance of density 2.6; it melts at 39° C. and boils at 230° C.,<sup>8</sup> with ammonia it forms  $\text{TiBr}_4 \cdot 8\text{NH}_3$ ,<sup>9</sup> and it is hydrolysed by water, forming

<sup>1</sup> Rosenheim and Schutte, *Zeitsch. anorg. Chem.*, 1901, 26, 239.

<sup>2</sup> Stahl and Wuthenow, *Ber.*, 1905, 38, 2619.

<sup>3</sup> Rosenheim and Schutte, *ibid.*

<sup>4</sup> Dilthey, *Lundén*, 1906, 344, 300.

<sup>5</sup> Stahl, *Ber.*, 1901, 37, 1105.

<sup>6</sup> Duppa, *J. prakt. Chem.*, 1838, 13, 158, 1839, 16, 345.

<sup>7</sup> Thorpe, *Trans. Chem. Soc.*, 1885, 47, 126.

<sup>8</sup> Duppa, *Proc. Roy. Soc.*, 1857, 8, 42.

<sup>9</sup> Ruff and Treidel, *Ber.*, 1912, 45, 1364.



oxybromides, of which two have been described,<sup>1</sup>  $\text{TiBr}_3\text{OH}$  and  $2\text{TiBr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ , a stable, crystalline powder.

**Hydrobromotitanic Acid,**  $\text{H}_2\text{TiBr}_6$ . The solution of titanium tetrabromide in water, alcohol, or ether is bright yellow, but in hydrobromic acid it is blood-red. The latter solution, therefore, contains a complex anion<sup>2</sup> which is probably  $(\text{TiBr}_6)''$ , to which there corresponds the ammonium salt  $(\text{NH}_4)_2\text{TiBr}_6 \cdot 2\text{H}_2\text{O}$  and the pyridine salt  $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{TiBr}_6$ , both of which consist of dark red crystals.

**Titanium Chlorobromides.** Two chlorobromides of titanium<sup>3</sup> -  $\text{TiCl}_2\text{Br}_2$ , boiling at  $176^\circ \text{C}$ ., and  $\text{TiClBr}_3$ , boiling at  $154^\circ \text{C}$ ., are said to have been obtained by the action of bromine on the di- and tri-chloride respectively, but whether they are single substances or mixtures is not yet certain.

#### IODIDES OF TITANIUM

The three iodides  $\text{TiI}_3$ ,  $\text{TiI}_4$ ,  $\text{TiI}_5$  are known.

**Titanium Di-iodide,**  $\text{TiI}_2$ , has been prepared by Defacqz and Copaux<sup>4</sup> by heating the tetra-iodide in mercury vapour conveyed in a current of hydrogen. It forms black, hygroscopic leaflets which are non-volatile and infusible and have a density of 4.3. It is insoluble in organic solvents, but decomposed by water and aqueous alkalis; boiling hydrochloric acid dissolves it, forming a blue liquid; aqueous ammonia forms the black hydroxide; heating in oxygen yields titanic oxide and iodine.

**Titanium Tri-iodide** has been obtained in the form of the hexahydrate  $\text{TiI}_3 \cdot 6\text{H}_2\text{O}$  by the electrolytic reduction of titanium tetra-iodide,  $\text{TiI}_4$ . It forms a very unstable, violet crystalline mass.

**Titanium Tetra-iodide (Titane Iodide),**  $\text{TiI}_4$ , is obtained when iodine vapour is passed over heated titanium,<sup>5</sup> when hydrogen iodide is passed into titanium tetrachloride while the latter is gradually raised to its boiling-point, and by the action of iodine vapour and hydrogen on titanium tetrachloride at a dull red heat.<sup>6</sup> Titane iodide forms a reddish brown, brittle, metallic-looking mass which melts at  $150^\circ \text{C}$ ., and then crystallises in large octahedra. It boils at  $360^\circ \text{C}$ ., forming an orange vapour, and distils unchanged. Its vapour density at  $140^\circ \text{C}$ . is 18.054 (air = 1) or 260 ( $\text{H} = 1$ ), indicating a molecular weight of 520, theory requiring 536. It fumes in the air, is combustible, and dissolves in water, forming a solution whence titanic acid soon separates by hydrolysis. Titane acid dissolves in hydriodic acid, forming a deep red solution which probably contains hydriodotitanic acid; the acid and its salts are, however, too unstable to be isolated.<sup>7</sup>

#### OXIDES AND HYDROXIDES OF TITANIUM

Titanium forms mono-, sesqui-, and di-oxides,  $\text{TiO}$ ,  $\text{Ti}_2\text{O}_3$ , and  $\text{TiO}_2$  respectively. To the monoxide there possibly corresponds a sulphate; the sesquioxide is basic, giving rise to salts; the dioxide is acidic.

<sup>1</sup> Rosenheim and Schutte, *Zeitsch. anorg. Chem.*, 1901, 26, 239

<sup>2</sup> Rosenheim and Schutte, *loc. cit.*

<sup>3</sup> Friedel and Guérin, *Compt. rend.*, 1875, 81, 889, 1876, 82, 509, 972.

<sup>4</sup> Defacqz and Copaux, *Bull. Soc. chim.* 1908, [iii], 839

<sup>5</sup> Moissan, *Compt. rend.*, 1895, 120, 290

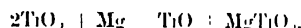
<sup>6</sup> Hautefeuille, *Compt. rend.*, 1863, 57, 151, 1864, 59, 189, 1867, 64, 704

<sup>7</sup> Rosenheim and Schutte, *loc. cit.*

forming titanates, but also possesses feebly basic properties and forms some salts.

In addition to these, several mixed or saline oxides have been described. The oxide  $\text{Ti}_2\text{O}_3$  or  $\text{TiO} \cdot \text{Ti}_2\text{O}_3$ , which may be called titanomagnetite, was obtained by Rose, and by Piccini and Marmo<sup>1</sup> by the dry reduction of titanic oxide,  $\text{TiO}_2$ ; whilst  $\text{Ti}_2\text{O}_3 \cdot \text{Ti}_2\text{O}_3 \cdot \text{TiO}_2$  is said to be formed when titanic oxide is heated in a reducing atmosphere with hydrogen chloride.<sup>2</sup> It has been alleged that  $\text{Ti}_7\text{O}_{12}$  is the final product of the reduction of titanic oxide by hydrogen, but the latter may be  $\text{Ti}_2\text{O}_3$ . Whether these supposed saline oxides are single substances or mixtures must be regarded as doubtful.

**Titanium Monoxide**,  $\text{TiO}$ , is formed, together with other products, when titanic oxide is heated with carbon or a metal such as zinc or magnesium; in the latter case titanate is also formed according to the reaction



which differs from the reaction of magnesium with silica owing to the inferior reducibility of titanic oxide.

Moissan<sup>3</sup> has obtained the monoxide in black prismatic crystals by heating titanic oxide with carbon in the electric furnace.

The hydroxide  $\text{Ti}(\text{OH})_2$  is formed as a black precipitate when alkali is added to a solution of titanium dihalide; it passes rapidly by oxidation into hydrated titanic oxide. According to Stahler<sup>4</sup> a sulphate corresponding to the monoxide is formed when titanium is dissolved in sulphuric acid.

**Titanium Sesquioxide**,  $\text{Ti}_2\text{O}_3$ , is formed, probably in an impure state, when the dioxide is ignited strongly in a current of hydrogen, and is obtained in the form of lustrous, copper-coloured crystals, together with the trichloride and oxychloride, when a mixture of hydrogen and titanium tetrachloride vapour is passed over the white-hot dioxide.<sup>5</sup>

When a microcosmic bead containing titanic oxide is heated in the reducing flame crystals of the sesquioxide separate.<sup>6</sup>

This oxide is isomorphous with Elba hematite<sup>7</sup>, and titanium iron ore,  $\text{FeTiO}_3$ , is on this account sometimes regarded as an isomorphous mixture of iron and titanium sesquioxides.

Titanium sesquioxide dissolves in concentrated sulphuric acid, forming a violet solution of the corresponding sulphate. The hydrated sesquioxide,  $\text{Ti}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , precipitated from a solution of the trichloride by alkali, may be black, red, brown, or dark blue. When suspended in water it constitutes a powerful reducing agent, even decomposing water, and being oxidised to the hydrated dioxide. When the hydrated sesquioxide is suspended in milk of lime and shaken with air, its oxidation is accompanied by an equivalent oxidation of water to hydrogen dioxide. A similar reaction occurs when chromic acid is added to titanium sesquioxide in presence of potassium iodide, the formation of titanic acid being accompanied by the liberation of an equivalent of iodine.<sup>7</sup>

<sup>1</sup> Piccini and Marmo, *Zeitsch. physikal. Chem.*, 1902, 32, 70.

<sup>2</sup> Friedel and Guerin, *Bull. Soc. chim.*, 1875, [n.] 23, 289, *Compt. rend.*, 1876, 82, 509.

<sup>3</sup> Moissan, *Compt. rend.*, 1892, 115, 1034.

<sup>4</sup> Stahler, *Ber.*, 1905, 38, 2619.

<sup>5</sup> Friedel and Guerin, *Compt. rend.*, 1875, 81, 889, 1876, 82, 509, 972.

<sup>6</sup> Braun, *Jahrb. Min.*, 1892, ii, 237.

<sup>7</sup> Manchot and Richter, *Ber.*, 1906, 39, 320, 488.

**Titanium Dioxide** (*Titanic Oxide*),  $\text{TiO}_2$ .—Titanium dioxide is naturally trimorphous, and occurs as the three minerals *rutile*, *anatase*, and *brookite*.

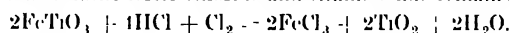
*Rutile*, the most important of the three, crystallises in tetragonal prisms, and has a density of 4.18 to 4.25. It is lustrous, of a reddish brown colour, has a hardness of 6 to 6.5 on Moh's scale, and is isomorphous with cassiterite ( $\text{SnO}_2$ ), zircon, and thorite.

*Anatase* is also tetragonal, but its crystals differ from those of *rutile*; it has a density of 3.82 to 3.95, a hardness of 5.5 to 6, and is brown or black in colour.

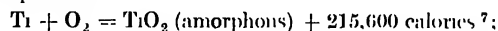
*Brookite* crystallises in rhombic prisms, having a density of 4.12 to 4.23 and a hardness of 5.5 to 6.

The three natural forms of titanic oxide are said to be isomorphous with stannic oxide.<sup>1</sup> They can all be produced artificially. *Rutile* is formed when amorphous titanium oxide is fused in a bead of borax,<sup>2</sup> microcosmic salt or potassium carbonate,<sup>3</sup> or melted with stannic oxide<sup>4</sup>; *anatase* is produced by the decomposition of titanium cyanonitride at red heat by water-vapour; *brookite* results when a mixture of titanium tetrachloride vapour, steam, and carbon dioxide is passed through a red-hot tube, and also when the vapour of titanium tetrachloride is decomposed by heated lime.<sup>5</sup> It has been shown by Lautfeulle<sup>6</sup> that anatase is the stable form of titanic oxide below 860° C., brookite between 860° C. and 1010° C., rutile above 1010° C.

Amorphous titanium dioxide may be obtained by precipitating in aqueous solution of titanic chloride with ammonia; by fusing finely powdered rutile or titanic iron ore with potassium carbonate, decomposing the resulting titanate with hydrofluoric acid in a platinum dish, separating and recrystallising the potassium titanfluoride formed, and decomposing its hot aqueous solution with ammonia; or by igniting titanic iron ore in a current of chlorine and hydrochloric acid, when the iron is eliminated as volatile ferric chloride and titanic oxide remains, thus:



Amorphous titanium dioxide is a white powder which, like stannic oxide, turns yellow and then brown when heated, and fuses in the oxyhydrogen flame. Its heat of formation when the metal is oxidised by sodium peroxide is:



and when the finely divided metal is burnt in oxygen, 218,100 calories.<sup>8</sup>

Titanic oxide is insoluble in water and dilute acids, but dissolves when heated with sulphuric acid, potassium hydrogen sulphate, or pyrosulphate, forming a sulphate of quadrivalent titanium.<sup>9</sup> It produces titanates when fused with alkalis or alkali carbonates. Thus titanic oxide possesses both basic and acidic properties, and so differs from silica, which is not basic.

<sup>1</sup> Wunder, *J. prakt. Chem.*, 1870, [ii], 2, 206

<sup>2</sup> Knop, *Jahrb. Min.*, 1877, 108

<sup>3</sup> Ebelmen, *Compt. rend.*, 1851, 32, 710

<sup>4</sup> Deville and Caron, *Annalen*, 1850, 108, 55.

<sup>5</sup> Daulric, *Compt. rend.*, 1849, 29, 227, 1850, 30, 383 1851, 39, 153

<sup>6</sup> Hautefeuille, *Ann. Chim. Phys.*, 1865, [iv], 4, 129

<sup>7</sup> Mixer, *Amer. J. Sci.*, 1909, [iv], 27, 393

<sup>8</sup> Mixer, *Amer. J. Sci.*, 1912, [iv], 33, 45.

<sup>9</sup> See Bornemann and Schirmeister, *Metallurgie*, 1910, 7, 646

**Titanic Hydroxides, the Titanic Acids.** The ortho- and meta-hydroxides,  $\text{Ti}(\text{OH})_4$  and  $\text{TiO}(\text{OH})_2$ , are generally believed to exist, and there are probably other hydroxides which are of the nature of condensed acids. There are no natural titanates which reach the degree of complexity shown by the natural silicates, neither is a form of titanate acid known which is definitely analogous to  $\beta$ -stannic acid,  $\text{Sn}_2\text{O}_3(\text{OH})_{10}$ ; nevertheless, as will appear, there is reason to believe that titanate acid may exist in complex molecules.

*Orthotitanic acid*,  $\text{Ti}(\text{OH})_4$ , is obtained as a voluminous, white precipitate when ammonia or alkali hydroxide or carbonate is added to a cold hydrochloric acid solution of a titanate. Whilst it remains fully hydrated it is soluble in dilute hydrochloric, sulphuric, and strong organic acids, forming the corresponding salts, but on heating it loses water and passes into more complex and less soluble hydrates. Even in contact with water it gradually passes into the meta-acid,<sup>1</sup> and on ignition forms the dioxide with evolution of light.

**Metatitanic Acid**,  $\text{TiO}(\text{OH})_2$ , insoluble in hydrochloric acid, is obtained by various means from hot solutions. Thus when an aqueous solution of titanate chloride is boiled the meta-acid is gradually precipitated; this precipitation takes place the more readily in presence of sulphuric acid or a soluble sulphate owing to the inferior stability of titanate sulphate; similarly, the soluble product of fusion of a titanate mineral with potassium hydrogen sulphate yields metatitanic acid when boiled with water. The hydrolysis of a slightly acidified solution of titanate sulphate which occurs on boiling is quantitative, and is employed for the estimation of titanium.

Metatitanic acid is also formed when a hot acid solution of a titanate compound is precipitated by alkali, as well as by the action of nitric acid of density 1.25 on metallic titanium. Although practically insoluble in dilute acids, metatitanic acid forms an opalescent, colloidal suspension with water, whence it is precipitated by acids and salt solutions. When ignited, the meta-acid passes into the anhydride without evolving light.

The assumption of the colloidal state by metatitanic acid suggests that the molecules of this substance are complex. Colloidal titanate acid has been obtained in other ways. On adding hydrochloric acid to the mass obtained by fusing titanate oxide with alkali, Rose<sup>2</sup> obtained a jelly consisting of the hydrated oxide, whilst Knop<sup>3</sup> found that the white precipitate formed on adding ammonia to a solution of titaniferous magnelite, in presence of tartaric acid added to keep the iron in solution, swelled to a transparent jelly when washed with water. Graham,<sup>4</sup> also, obtained colloidal titanate acid as a hydrosol, by the dialysis of a hydrochloric acid solution of the ortho-acid, and this on concentration yields a hydrogel.<sup>5</sup> Thus it appears that in its colloidal properties titanate acid closely resembles silicic acid; moreover, the question arises whether the simple formulae  $\text{Ti}(\text{OH})_4$  and  $\text{TiO}(\text{OH})_2$  can properly be applied to the two hydrates of titanate oxide which are respectively soluble and insoluble in hydrochloric acid, or whether the molecules of these two

<sup>1</sup> Wagner, *Ber.*, 1888, 21, 960.

<sup>2</sup> Rose, *Gilbert's Annalen*, 1823, 73, 76.

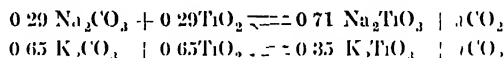
<sup>3</sup> Knop, *Annalen*, 1862, 123, 351.

<sup>4</sup> Graham, *Pogg. Annalen*, 1864, 123, 529.

<sup>5</sup> Von den Pfordten, *Annalen*, 1887, 237, 213.

substances, being very complex, approximate to rather than correspond exactly in composition with these formulae. According to Carnelley and Walker,<sup>1</sup> who have examined the influence of the gradual increase of temperature upon these and other hydrates, the regular form of the curves obtained with titanic as well as silicic hydrate is against the existence of definite hydrates of any evident degree of stability.

**The Titanates.**—It has already been seen that titanic hydroxide is amphoteric, dissolving in strong acids to form salts of these acids, and in strong alkalis to form titanates. Titanic hydroxide is thus an acid of the weakest description, and is unable to displace carbonic acid from aqueous solutions of carbonates. Alkali titanate, however, is formed when titanic oxide is fused with alkali carbonate, and the reaction is reversible when the fusion is carried out in an atmosphere of carbon dioxide, the conditions of equilibrium at 900–1100° C. and 1 atmosphere CO<sub>2</sub> being represented by the following equations<sup>2</sup>:



Titanic oxide resembles silica in its power of displacing carbon dioxide, and this power diminishes through zirconium to thorium with increase in the basic power of the dioxide.

Certain mineral titanates are known, and can be prepared artificially.

*Perofskite* is calcium metatitanate, CaTiO<sub>3</sub>, containing small quantities of ferrous, manganese, and magnesium oxides; it occurs in the Urals and Arkansas in yellow to iron-black rhombic crystals, having a density of 4.0 and hardness 5.5 on Moh's scale, and can be produced artificially by the strong ignition of a mixture of titanic oxide, lime, and potassium carbonate.<sup>3</sup>

*Ilmenite* or titanic iron is ferrous metatitanate, FeTiO<sub>3</sub>, it occurs in Norway, Canada, and elsewhere in black rhombohedral crystals, having a sub-metallic lustre, density 4.5 to 5, and hardness 5 to 6 (Moh's scale).

*Pyrophanite*, isomorphous with ilmenite, is MnTiO<sub>3</sub>, and *gehlenite* is MgTiO<sub>3</sub>.

*Pseudobrookite* is ferric orthotitanate, Fe<sub>2</sub>(TiO<sub>3</sub>)<sub>3</sub>, it consists of brown or black orthorhombic crystals of density 4.39 and hardness 6 (Moh's scale).

*Titanite* or *sphene*, calcium titaंसilicate, CaTiSiO<sub>5</sub>, may be regarded as the calcium salt of dimetasilicic acid, H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, in which a molecule of silica has been exchanged for one of titanic oxide. It occurs, embedded in granite, gneiss, and mica-schist, in yellow, green, red, grey, brown, or black monoclinic crystals of density 3.51 and hardness 5 to 5.5 (Moh's scale). It has been obtained artificially by fusing together a mixture of silica, titanic oxide, and calcium chloride.<sup>4</sup>

Titanic oxide is known partially to replace silica in such minerals as biotite, augite, and olivine; and, according to Groth,<sup>5</sup> the oxides ZrO<sub>2</sub>, ThO<sub>2</sub> and SnO<sub>2</sub> may also replace silica isomorphously. Neither

<sup>1</sup> Carnelley and Walker, *Trans. Chem. Soc.*, 1888, 53, 82.

<sup>2</sup> D. P. Smith, *Zeitsch. anorg. Chem.*, 1903, 37, 532.

<sup>3</sup> Ebelmen, *Compt. rend.*, 1851, 32, 710.

<sup>4</sup> Hautefeuille, *Ann. Chim. Phys.*, 1865, [ser. 4], 4, 129.

<sup>5</sup> Groth, *Tabellar. Übersicht d. Miner.*, 1898, 113.

titanic oxide nor any of these other oxides is known, however, to form such complex acids as are formed by silica.

Alkali titanates may be prepared by fusion, by boiling titanic acid with aqueous alkali, or by precipitating a hydrochloric acid solution of titanic acid with alkali carbonate. Thus potassium metatitanate,  $K_2TiO_3$ , is obtained as a yellow, fibrous mass when titanic oxide is fused with potassium carbonate; the hydrated salt  $K_2TiO_3 \cdot 11H_2O$  crystallises on evaporating a solution of titanic acid in caustic potash; the trititanate  $K_2Ti_3O_7 \cdot 2H_2O$  is precipitated by potassium carbonate from a hydrochloric acid solution of titanic acid, whilst  $K_2Ti_4O_7 \cdot 3H_2O$  is formed when  $K_2TiO_3$  is boiled with water, and the hexatitanate  $K_2Ti_6O_{11} \cdot 2H_2O$  is produced by the action of hydrochloric acid on the dihydrated trititanate.

The three sodium salts,  $Na_2Ti_2O_5$ ,  $Na_2TiO_3$ ,  $Na_4Ti_3O_8$ , all of which are crystalline but insoluble in water, are produced by the fusion of titanic oxide with sodium carbonate, together with sodium tungstate, to promote crystallisation, and treatment of the cooled product with water.

In addition to these alkali salts and artificial minerals, a number of meta-, ortho-, and poly-titanates of other metals have been prepared, generally by fusing titanic oxide with the carbonate, chloride, or sulphate of the metal. They are as follows:  $Sr_2Ti_2O_7$ ,  $Ba_2Ti_2O_7$ ,  $Mg_2TiO_4$ ,  $MgTiO_3$ ,  $Zn_2TiO_4$ ,  $ZnTiO_3$ ,  $ZnTi_2O_7$ ,  $Zn_3Ti_2O_7$ ,  $Zn_4Ti_5O_{11}$ ,  $Mn_2TiO_4$ ,  $MnTiO_3$ ,  $CoTiO_3$ ,  $NiTiO_3$ ,  $Fe_2TiO_5$ ,  $FeTiO_3$ .

## TITANIUM AND SULPHUR

**Titanium Sulphides.** Three sulphides of titanium are known, corresponding to the three degrees of valency shown by this element. They are  $TiS$ ,  $Ti_2S_3$ ,  $TiS_2$ .

**Titanium Monosulphide,  $TiS$ ,** is formed by the reduction of the sesquioxide or disulphide in a current of hydrogen. The reaction takes place at the softening temperature of glass; and the monosulphide is a reddish, lustrous, metallic-looking solid, resembling bismuth. It is stable in the air at ordinary temperature, but burns when heated, forming titanic oxide. It is unattacked by dilute hydrochloric and sulphuric acids, slowly oxidised by nitric acid and aqua regia, and dissolved by concentrated sulphuric acid.

**Titanium Sesquisulphide,  $Ti_2S_3$ ,** is produced when titanic oxide is heated to bright redness in a stream of moist sulphuretted hydrogen and carbon disulphide vapour<sup>1</sup>; when the nitride,  $TiN$ , is heated in a mixture of sulphur vapour and hydrogen<sup>2</sup>, and also when the disulphide,  $TiS_2$ , is ignited in an indifferent atmosphere. Titanium sesquisulphide is a metallic, greyish black, crystalline powder which is stable towards dilute acids and alkalis, but dissolves in concentrated sulphuric and nitric acids, forming green solutions of unknown composition.

**Titanium Disulphide,  $TiS_2$ ,** is formed in a crude state by the action of carbon disulphide vapour on titanic oxide,<sup>3</sup> and also by heating

<sup>1</sup> Cornu and Gautier, *Compt. rend.*, 1892, 115, 823.

<sup>2</sup> Thorpe, *Trans. Chem. Soc.*, 1885, 47, 191.

<sup>3</sup> Schneider, *Zeitsch. anorg. Chem.*, 1895, 8, 81.

<sup>4</sup> Rose, *Gilbert's Annalen*, 1893, 73, 67, 129.

together a mixture of rutile ( $\text{TiO}_2$ ), sulphur, sodium carbonate, and carbon<sup>1</sup>; it is obtained in a pure state, in the form of yellow, lustrous scales resembling pyrites, when a mixture of hydrogen sulphide and titanium tetrachloride (Ebelmen) or tetrafluoride<sup>2</sup> is passed through a strongly heated porcelain tube. Titanium disulphide resembles the other sulphides in its behaviour towards acids; boiling caustic potash decomposes it, forming potassium sulphide and titanate; it possesses, however, no thio-anhydride properties since it does not dissolve in alkali sulphide solution.

**Titanium Sulphates.** Titanium is sharply separated from silicon as well as from germanium by its power of forming the sulphates  $\text{Ti}_2(\text{SO}_4)_3$ ,  $\text{Ti}(\text{SO}_4)_2$ , and perhaps  $\text{TiSO}_4$ , as well as basic and double or complex sulphates.

**Titanous Sulphate,**  $\text{TiSO}_4$ , is formed, according to Stahler,<sup>3</sup> when titanium is dissolved in sulphuric acid and the solution is evaporated.

**Titanium Sesquisulphate,**  $\text{Ti}_2(\text{SO}_4)_3$ .—According to Glatzel<sup>4</sup> the octahydrate  $\text{Ti}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  is obtained by dissolving the metal in dilute sulphuric acid, and evaporating the solution. A violet solution is said to be formed which on being concentrated becomes blue and deposits tufted crystals. According to Stahler and Wirthwein,<sup>5</sup> however, the sesquisulphate is not formed in this way; but when a concentrated solution of the trichloride is repeatedly evaporated at 60° C. with dilute sulphuric acid in a vacuum, a crystalline precipitate of titanium sesquisulphate sulphuric acid is formed, which, after washing with acetic acid and ether, has the composition  $3\text{Ti}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 25\text{H}_2\text{O}$ . The same product is obtained as a violet crystalline powder when titanous sulphate dissolved in 50 per cent. sulphuric acid is reduced electrolytically for five or six hours. The anhydrous sesquisulphate,  $\text{Ti}_2(\text{SO}_4)_3$ , is separated as a green, crystalline powder, insoluble in water, alcohol, ether or concentrated sulphuric acid, by the repeated evaporation of a dilute sulphuric acid solution of titanium sesquisulphate sulphuric acid in absence of air. Titanium sesquisulphate closely resembles the corresponding vanadium sulphate,  $\text{V}_2(\text{SO}_4)_3$ , in properties, and in the compounds it forms with sulphuric acid and other sulphates; it is decomposed by heat into  $\text{SO}_2$ ,  $\text{SO}_3$ , and  $\text{TiO}_2$ .

**Double or Complex Sulphates of Tervalent Titanium.** The above compound of titanium sesquisulphate and sulphuric acid may be alternatively described as titanousulphuric acid; the alkali salts of this acid will then be complex rather than double salts. By combination with rubidium and ammonium sulphates the following titanousulphates have been obtained by Stahler<sup>6</sup>:  $3\text{Ti}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ;  $3\text{Ti}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$ . In addition to these a sodium salt of the composition  $\text{Ti}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ <sup>7</sup> has been obtained in violet crystals by the electrolytic reduction of sodium titanous sulphate

<sup>1</sup> Berthier, *Gmelin-Kraut, Handb.*, 1897, n. 2, 2

<sup>2</sup> Ruff and Ipsen, *Ber.*, 1903, 36, 1777

<sup>3</sup> Stahler, *Ber.*, 1905, 38, 2619

<sup>4</sup> Glatzel, *Ber.*, 1876, 9, 1829.

<sup>5</sup> Stahler and Wirthwein, *loc. cit.*

<sup>6</sup> Stahler, *loc. cit.*

<sup>7</sup> Knecht, *Ber.*, 1903, 36, 166.

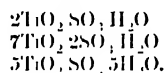
solution. It is prepared technically and used as a reducing agent.<sup>1</sup> Perchlorates can be reduced and estimated by its means.<sup>2</sup>

Besides these salts titanium sesquisulphate forms alums, which, like other alums, diminish in solubility with increase in electropositivity of the alkali metal. The rubidium and caesium salts,  $\text{Rb}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  and  $\text{Cs}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  have been prepared by Piccini.<sup>3</sup>

**Titanic Sulphates.** The metallic nature of titanium is emphasised by the existence of sulphates corresponding to the dioxide  $\text{TiO}_2$ . The normal disulphate is said to exist, and there are several basic sulphates as well as salts of titansulphuric acids.

**Normal Titanic Sulphate,**  $\text{Ti}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , has been described by Glatzel<sup>4</sup> as a yellow, amorphous mass obtained by oxidising the sesquisulphate with nitric acid and evaporating the resulting solution. According to more recent observers, however, the existence of this compound is doubtful.

The *first basic sulphate*,  $\text{Ti}_2\text{O}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ , or  $2\text{TiO}_2 \cdot 3\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , is formed in crystals, according to Blondel,<sup>5</sup> when a sulphuric acid solution of titanic acid is heated to  $120^\circ \text{C}$ . The *second basic sulphate*, titanyl sulphate,  $\text{TiOSO}_4$ , was first obtained by Merz<sup>6</sup> as a white powder by rapidly evaporating a sulphuric acid solution of titanic acid, and by Blondel in crystals by heating a similar solution to  $225^\circ \text{C}$ . The hydrate  $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$  was also obtained by the use of somewhat diluted sulphuric acid, and the following hydrated basic salts by further modifying the temperature and dilution:



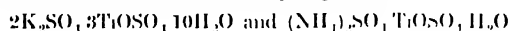
Pentahydrated titanyl sulphate,  $\text{TiOSO}_4 \cdot 5\text{H}_2\text{O}$ , was obtained by Rosenheim and Schütte<sup>7</sup> by boiling titanic acid with alcoholic sulphuric acid and then evaporating off the alcohol and precipitating with ether.

**Complex Titani- and Titanyl-sulphates.** Titanic sulphate and titanyl sulphate combine with certain normal sulphates to form complex salts.

**Potassium Titanisulphate,**  $\text{K}_2\text{Ti}(\text{SO}_4)_4$ , is produced by melting together titanic oxide and potassium pyrosulphate.

The alkaline earth salts<sup>8</sup>  $\text{CaTi}(\text{SO}_4)_4$ ,  $\text{SrTi}(\text{SO}_4)_4$ , and  $\text{Ba}_2\text{Ti}_2(\text{SO}_4)_9$ , are formed when  $\text{TiO}_2$  dissolved in concentrated sulphuric acid is mixed with a sulphuric acid solution of the corresponding sulphate and the resulting solution is concentrated. These salts are decomposed by water with precipitation of titanic acid.

**Potassium and Ammonium Titanylsulphates,**



respectively, have been obtained by adding concentrated aqueous

<sup>1</sup> Spence and Sons, D.R.P., 119,602.

<sup>2</sup> Stahlcr, *Chem. Zvt.*, 1900, 33, 759.

<sup>3</sup> Piccini, *Gi. Ita.*, 1895, 25, [iii], 512. *Zeitsch. anorg. Chem.*, 1898, 17, 355.

<sup>4</sup> Glatzel, *Ber.*, 1876, 9, 1829.

<sup>5</sup> Blondel, *Bull. Soc. chim.*, 1899, [iii], 21, 262.

<sup>6</sup> Merz, *J. prakt. Chem.*, 1866, 99, 157.

<sup>7</sup> Rosenheim and Schütte, *Zeitsch. anorg. Chem.*, 1901, 26, 239.

<sup>8</sup> Weinland and Kuhl, *Zeitsch. anorg. Chem.*, 1907, 54, 253.



solutions of the corresponding sulphates to a saturated solution of titanous acid in sulphuric acid.<sup>1</sup> These salts are soluble in cold water, but titanous acid gradually separates from their solutions.

The following compounds of titanous oxide with selenous and selenic acids have been obtained<sup>2</sup>:  $\text{TiO}_2 \cdot \text{SeO}_2 \cdot \text{H}_2\text{O}$ ,  $2\text{TiO}_2 \cdot \text{SeO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{TiO}_2 \cdot \text{SeO}_3 \cdot \text{H}_2\text{O}$ ,  $2\text{TiO}_2 \cdot \text{SeO}_3 \cdot \text{H}_2\text{O}$ .

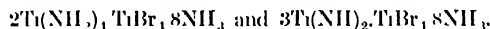
### TITANIUM AND NITROGEN

A characteristic of titanium is its proneness to combine with nitrogen to form a nitride. Such a compound was obtained many years ago by heating  $\text{TiCl}_4$  with  $\text{NH}_3$  alone or in a current of ammonia<sup>3</sup>; it was copper-coloured and was mistaken for the element until Wohler<sup>4</sup> proved that it contained nitrogen and assigned to it the formula  $\text{Ti}_3\text{N}_4$ . Wohler also obtained a dark blue substance with a coppery lustre, to which he attributed the formula  $\text{TiN}_2$ , by igniting titanous oxide in a current of ammonia. Schneider,<sup>5</sup> however, showed that the supposed nitride  $\text{Ti}_3\text{N}_4$  contained oxygen; and he was unable to obtain Wohler's dinitride, whose existence had previously been denied by Friedel and Guérin.<sup>6</sup> Until recently, therefore, the existence of only one nitride of titanium,  $\text{TiN}$  or  $\text{Ti}_2\text{N}_3$ , was recognised<sup>7</sup>; but titanous nitride,  $\text{Ti}_3\text{N}_4$ , has now been obtained by Ruff and Treidel.<sup>8</sup>

**Titanous Nitride**,  $\text{TiN}$  or  $\text{Ti}_2\text{N}_3$ , was obtained by Moissan by heating titanous oxide with or without carbon in a graphite crucible in presence of nitrogen, and also by Ruff and Eisner<sup>7</sup> by heating Wohler's supposed  $\text{Ti}_3\text{N}_4$  in a current of ammonia at  $1500^\circ \text{C}$ . for six hours till all the chlorine and oxygen it contained were removed. It is, however, best prepared by heating the dioxide with ammonia in a porcelain tube for four to six hours at  $1400$ – $1500^\circ \text{C}$ .<sup>9</sup>

The nitride obtained by Moissan was a bronze-yellow mass having a density of 5.18, and was hard enough to scratch rubies and cut diamonds; that obtained by Ruff and Eisner was bronze-coloured and had a density of 5.10 at  $18^\circ \text{C}$ .

**Titanous Nitride**,  $\text{Ti}_3\text{N}_4$ , was obtained by Ruff and Treidel<sup>10</sup> in the following way. When titanium tetrabromide ammonia,  $\text{TiBr}_4 \cdot 8\text{NH}_3$ , was washed with liquid ammonia an orange-coloured, insoluble substance was obtained having a composition between



When this product was treated with a solution of an equivalent amount of potassium amide in liquid ammonia a mixture was formed containing 20 per cent. of the original bromide, 10 per cent. of potassium hydrogen titanium di-nitride,  $\text{Ti}(\text{NH})\text{NK}$ , and 70 per cent. of titanous nitride,  $\text{Ti}_3\text{N}_4$ . This latter compound has a brown colour, is decomposed by

<sup>1</sup> Rosenheim and Schütte, *Zeitsch. anorg. Chem.*, 1901, 26, 239.

<sup>2</sup> Breck, *Zeitsch. anorg. Chem.*, 1913, 80, 418.

<sup>3</sup> Liebig, *Pogg. Annalen*, 1830, 21, 259.

<sup>4</sup> Wohler, *Annalen*, 1850, 73, 31.

<sup>5</sup> Schneider, *Zeitsch. anorg. Chem.*, 1895, 8, 81.

<sup>6</sup> Friedel and Guérin, *Ann. Chim. Phys.*, 1876, [v], 7, 24.

<sup>7</sup> Ruff and Eisner, *Ber.*, 1908, 41, 2250.

<sup>8</sup> Ruff and Treidel, *Ber.*, 1912, 45, 1364.

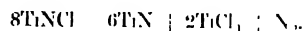
<sup>9</sup> Ruff, *Ber.*, 1909, 42, 900.

<sup>10</sup> Ruff and Treidel, *loc. cit.*

heat into titanous nitride,  $TiN$ , and nitrogen, and by water into hydrated titanate oxide and ammonia.

**Titanamide.** According to Bly and Wibelauer,<sup>1</sup> and Stahler,<sup>2</sup> titanamide,  $Ti(NH_2)_3$ , is formed when  $TiCl_3 \cdot 6NH_3$  or  $TiCl_3 \cdot 8NH_3$  is extracted with liquid ammonia. Ruff and Eisner,<sup>3</sup> however, deny that this compound is so formed.

**Titanium Nitrogen Halides.** Ruff and Eisner<sup>3</sup> found that when  $TiCl_3 \cdot 6NH_3$  is extracted with liquid ammonia a complex chloramide is formed, which when carefully heated in a vacuum at  $270^\circ C$  leaves impure titanium nitrogen chloride,  $TiNCl$ , as a dirty green residue. This substance reacts vigorously with water, forming ammonium chloride, nitrogen, and titanium dioxide. On being strongly heated it decomposes thus:



Titanium nitrogen bromide,  $TiNBr$ , was obtained in a pure state in a similar way, the residue from the ammonia extraction being heated at  $200^\circ C$ , under 1 mm. pressure. It reacts with water similarly to the chloride.

The contrast between the behaviour of silicon and titanium halides towards ammonia is noteworthy. Silicon easily loses all its halogen; titanium, in accordance with its more electropositive character, retains one halogen atom in the compounds  $TiNCl$  and  $TiNBr$ , to which silicon presents no analogy.

**Titaninitric Acid.** By evaporating a nitric acid solution of titanate acid over lime Merz<sup>4</sup> obtained crystals of the composition  $5TiO_2 \cdot N_2O_5 \cdot 6H_2O$ ; no salts of this complex acid are known.

## TITANIUM AND PHOSPHORUS

**Titanium Phosphide.** When hydrogen phosphide acts upon cold titanate chloride a yellow, crystalline substance is obtained which on heating yields hydrogen phosphide and hydrogen chloride, and leaves a residue of titanium phosphide,<sup>5</sup>  $TiP$ , as a brittle mass with metallic lustre and density of 3.95. This substance is insoluble in dilute and concentrated acids and alkalis, but burns in air and when heated in chlorine forms a yellow sublimate of  $TiCl_4 \cdot PCl_5$ .

**Titanophosphoric Acid and its Salts.** Merz<sup>6</sup> obtained a titanophosphoric acid, or titanate phosphate, of the composition  $2TiO_2 \cdot P_2O_5 \cdot 4H_2O$  by precipitating titanate chloride solution with a soluble phosphate and thoroughly washing the product. A similar substance was obtained by Wehrm and Giraud<sup>7</sup>; and by heating together titanate and phosphoric acids, as well as by melting  $TiO_2$  with sodium or potassium metaphosphate,<sup>8</sup> the crystalline compound  $TiO_2 \cdot P_2O_5$  is formed. The

<sup>1</sup> Bly and Wibelauer, *Ber.*, 1903, 36, 1228.

<sup>2</sup> Stahler, *Ber.*, 1905, 38, 2619.

<sup>3</sup> Ruff and Eisner, *Ber.*, 1908, 41, 2250.

<sup>4</sup> Merz, *J. prakt. Chem.*, 1866, 99, 157.

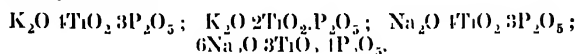
<sup>5</sup> Gewecke, *Annalen*, 1908, 361, 79.

<sup>6</sup> Merz, *loc. cit.*

<sup>7</sup> Wehrm and Giraud, *Compt. rend.*, 1877, 85, 289.

<sup>8</sup> Ouyard, *Compt. rend.*, 1890, 111, 177.

following crystallised alkali salts of titaniphosphoric acid have been obtained by Ouyard<sup>1</sup>:



#### TITANIUM AND CARBON

**Titanium Carbide, TiC,** is obtained in an impure state, in the form of steel-grey crystals, from cast-iron smelted from ores containing titanium.<sup>2</sup> It was obtained by Moissan<sup>3</sup> by heating together a mixture of 160 parts of titanate acid and 70 parts of carbon, and formed a crystalline mass resembling metallic titanium and having a density of 4.25. It does not, however, dissolve in hydrochloric acid, nor decompose steam at 700° C., but dissolves slowly in aqua regia.

**Titanium Cyanonitride.**—Very hard cubical crystals of a bright copper colour are sometimes found in the cavities of cast-iron and slag obtained by the smelting of titaniferous iron ore in the blast-furnace. This substance was mistaken by Wollaston<sup>4</sup> for metallic titanium, but Wohler proved that it contained carbon and nitrogen, and attributed to it the formula  $\text{Ti}(\text{CN})_2 \cdot 3\text{Ti}_2\text{N}_2$ . Wohler<sup>5</sup> also obtained this substance artificially by strongly heating in a closed crucible a mixture of potassium ferrocyanide and titanate oxide, and by bringing titanium tetrachloride vapour into contact with fused potassium cyanide; it is also formed<sup>6</sup> when a stream of nitrogen is passed over a white-hot mixture of titanate oxide and charcoal. Cyanonitride of titanium has a density of 5.28 (Wollaston) or of 4.1 to 5.1.<sup>7</sup> It is unattacked by boiling nitric or sulphuric acid, but easily dissolved by a mixture of nitric and hydrofluoric acids. That it contains the cyanogen radical is shown by the fact that when heated in a current of chlorine it forms a compound of titanium tetrachloride and cyanogen chloride,  $\text{TiCl}_4 \cdot \text{CNCl}$ , which appears as a sublimate, and when ignited in a current of steam yields hydrogen, hydrogen cyanide and ammonia, leaving a residue of titanate oxide. When this substance is fused with potash, ammonia is evolved and titanate formed. Its composition cannot be regarded as settled; whether it is really titanium "cyanonitride" or a mixture of carbide and nitride may even be uncertain,<sup>8</sup> though it differs from nitride in yielding the  $\text{TiCl}_4 \cdot \text{CNCl}$  compound when heated with chlorine.

**Titanium Thiocyanates.**—The complex thiocyanates of trivalent titanium,  $\text{K}_3\text{Ti}(\text{SCN})_6 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_3\text{Ti}(\text{SCN})_6 \cdot 6\text{H}_2\text{O}$ , exist; as well as thiocyanates of the quadrivalent metal.

When a 10 per cent. solution of thiocyanic acid is saturated with titanate acid, and evaporated over sulphuric acid, titanylthiocyanate,  $\text{TiO}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ , separates as a brownish red crystalline powder. The potassium salt,  $\text{K}_2\text{TiO}(\text{SCN})_4 \cdot \text{H}_2\text{O}$ , of the unknown complex

<sup>1</sup> Ouyard, *Compt. rend.*, 1890, **III**, 177.

<sup>2</sup> Shiner, *Chem. News*, 1887, **55**, 156.

<sup>3</sup> Moissan, *Compt. rend.*, 1895, **120**, 290, 1897, **125**, 839.

<sup>4</sup> Wollaston, *Phil. Trans.*, 1823, 17.

<sup>5</sup> Wohler, *Annalen*, 1850, **73**, 34, 74, 212.

<sup>6</sup> Wohler and Deville, *Annalen*, 1857, **103**, 230.

<sup>7</sup> Hogg, *Chem. News*, 1893, **68**, 163.

<sup>8</sup> Joly, *Compt. rend.*, 1876, **82**, 1195.

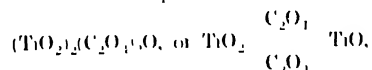
titanylthiocyanic acid,  $\text{H}_2\text{TiO}(\text{SCN})_2$ , is formed by the combination of potassium thiocyanate with titanylthiocyanate. It forms deep red rhombic crystals, soluble in but slowly decomposed by water. The corresponding ammonium, sodium, barium, pyridine, and quinoline salts have also been obtained.<sup>1</sup> Titanic thiocyanurate,  $\text{Ti}(\text{H}_2\text{S}_3\text{C}_3\text{N}_3)_3$ , also exists.

**Titanium Salts of Organic Acids.** A formate, double formates with the alkali metals,<sup>2</sup> and a complex basic acetate of tervalent titanium exist; and one of the corresponding oxalates have been prepared by Stahlcr.<sup>3</sup>

**Titanium Sesquioxalate,**  $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ , crystallises in yellow prisms, soluble in water, when alcohol is added a solution of titanium trichloride mixed with excess of oxalic acid. The following double salts have also been obtained:  $\text{TiNH}_4(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{TiK}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{TiRb}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , and the colour of their solutions show that they contain complex anions.

The following **oxalates of quadrivalent titanium** have been prepared. Hydrated titanyl oxalate,  $\text{TiOC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , has been obtained in an uncrystallised condition by dissolving titanous acid in concentrated aqueous oxalic acid solution; if, however, titanous acid is boiled with alcoholic oxalic acid, and the solution precipitated with ether,  $\text{TiOC}_2\text{O}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  is formed as a crystalline precipitate, soluble in water and alcohol, whilst the more basic salt,  $\text{Ti}_2\text{O}_3 \cdot \text{C}_2\text{O}_4 \cdot 12\text{H}_2\text{O}$ , is precipitated by alcohol from a concentrated solution of oxalic acid mixed with one of titanous acid in hydrochloric acid.<sup>4</sup>

Titanyloxalic acid,  $\text{H}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ , is obtained in long needles, soluble in water and alcohol, by decomposing its barium salt,  $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , with sulphuric acid and evaporating the resulting solution<sup>5</sup>; the potassium and ammonium salts,  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ , have also been obtained crystalline. A peroxidised oxalate of the composition



has been obtained by Mazzucchelli and Pantanelli.<sup>6</sup>

**Titantartarates and Allied Salts.** Titanous hydroxide dissolves in a concentrated solution of tartaric acid, and alcohol precipitates from this solution the tartarate  $\text{TiC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ; whilst solutions of alkali hydrogen tartarates dissolve the same hydroxide and form gelatinous substances of the composition  $2\text{M}_2\text{O} \cdot 2\text{TiO}_2 \cdot 3\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ . The basic tartarate  $\text{Ti}_2\text{O}_3 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 7\text{H}_2\text{O}$  has also been obtained.<sup>7</sup> The titantartarates, as well as many other salts of complex acids formed by the combination of feebly acidic oxides with organic hydroxy-acids, have been studied by Henderson, Orr, and Whitehead<sup>8</sup> who record the previous preparation of titantartarates,  $\text{TiO} \cdot \text{C}_6\text{H}_6\text{O}_7\text{M}'_2$ , titantar-

<sup>1</sup> Rosenheim and Cohn, *Zets. angew. Chem.*, 1901, 28, 167.

<sup>2</sup> Stahlcr and Bachman, *Ber.*, 1911, 44, 2906.

<sup>3</sup> Stahlcr, *Ber.*, 1905, 38, 2619.

<sup>4</sup> Rosenheim and Schotté, *Zets. angew. Chem.*, 1901, 26, 249.

<sup>5</sup> Péchard, *Compt. rend.*, 1894, 116, 1313.

<sup>6</sup> Mazzucchelli and Pantanelli, *Atti R. Accad. Lincei*, 1909 [5], 18, 1, 518.

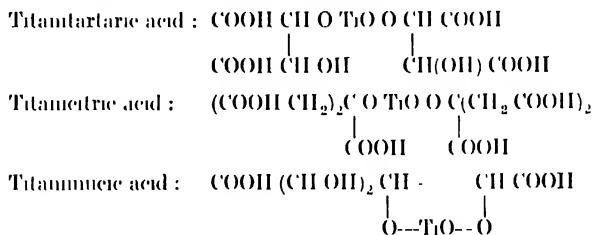
<sup>7</sup> Rosenheim and Schotté, *ibid.*

<sup>8</sup> Henderson, Orr, and Whitehead, *Trans. Chem. Soc.*, 1899, 75, 542.

trates,  $\text{TiO}(\text{C}_4\text{H}_4\text{O}_6\text{M}')_2$  and  $\text{TiO}:\text{C}_4\text{H}_3\text{O}_6\text{M}'$ , and titanumates,  $\text{TiO}:\text{C}_6\text{H}_7\text{O}_8\text{M}'$ , and have obtained the following salts in a pure, crystalline state:

Sodium titaantetratrate	$\text{TiO}(\text{C}_2\text{H}_3\text{O}_6\text{Na})_2 \cdot 8\text{H}_2\text{O}$
Potassium ..	$2\text{TiO}(\text{C}_2\text{H}_3\text{O}_6\text{K})_2 \cdot 9\text{H}_2\text{O}$
Ammonium ..	$2\text{TiO}(\text{C}_2\text{H}_3\text{O}_6\text{NH}_4)_2 \cdot 7\frac{1}{2}\text{H}_2\text{O}$
Barium ..	$\text{TiO}(\text{C}_2\text{H}_3\text{O}_6)_2 \cdot \text{Ba} \cdot 5\frac{1}{2}\text{H}_2\text{O}$
Potassium titanate	$\text{TiO}(\text{C}_2\text{H}_3\text{O}_7\text{K})_2 \cdot \text{H}_2\text{O}$
Potassium titanumate	$\text{TiO} \cdot \text{C}_6\text{H}_5\text{O}_8\text{K} \cdot 3\text{H}_2\text{O}$

All these salts are prepared by dissolving titanium hydroxide in a solution of the corresponding metal hydrogen salt of the hydroxy-acid. They are thus analogous to tartar emetic; and the constitutions of the complex acids may thus be represented:



Since these acids contain the radicle  $\text{TiO}''$ , the prefix titanyl- is perhaps preferable to titan-. A peroxidised titantartarate of the composition  $\text{TiO}_3 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{C}_2\text{H}_3\text{O}_6 \cdot \text{K} 9\text{H}_2\text{O}$  has also been prepared.<sup>1</sup>

## TITANIUM AND SILICON

**Titanium Silicide.**—Possibly the silicide  $\text{Ti}_3\text{Si}$  exists as well as the disilicide  $\text{TiSi}_2$ . The latter has been prepared by igniting in a crucible a mixture of 200 grams of aluminum powder, 250 grams of sulphur, 180 grams of fine sand, and 15 grams of titanous acid or 1 gram of potassium titanfluoride, the whole being covered with a layer of magnesium powder.<sup>2</sup>

Titanium silicide,  $\text{TiSi}_2$ , consists of small grey, tetragonal pyramids of density 4.02 and hardness 4.5 on Moh's scale; it is insoluble in mineral acids, except hydrofluoric acid, but dissolves slowly in 10 per cent. potassium hydroxide solution.

## PERTITANIC ACID AND THE PERTITANATES

It was observed by Schone<sup>3</sup> that the addition of hydrogen peroxide to a titanous solution produces a yellow colour. There are thus produced compounds of titanium superoxide,  $\text{TiO}_4$ . This oxide is best produced.<sup>1</sup>

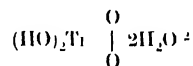
<sup>1</sup> Mazzucchelli and Pantanelli, *Atti R. Accad. Lincei*, 1909, [v], 18, 1, 518; *Gazzetta*, 1910, 40, 1, 666.

<sup>2</sup> Honigschmid, *Compt rend*, 1906, 143, 224

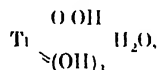
<sup>1</sup> Schöne, *Dingler's Poly. J.*, 1873, **210**, 317.

<sup>4</sup> *Classen. Ber.*, 1888, 21, 370, Melikoff and Pissarjewski, *Ber.*, 1898, 31, 679.

in a hydrated form, by slowly adding titanous chloride to dilute alcohol, followed by a large excess of hydrogen peroxide and then ammonia or other alkali. A reddish yellow liquid is thus produced from which a yellow precipitate gradually separates, which when dried corresponds approximately to the formula  $\text{TiO}_3 \cdot 3\text{H}_2\text{O}$ <sup>1</sup>. The question whether this compound may be really  $\text{TiO}_3 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$  is to be answered in the negative by reason of the fact that its solution does not show the reaction with chromic acid characteristic of hydrogen peroxide, and also because of the existence of the fluoroxypertitanates (*q.v.*) which are anhydrous derivatives of  $\text{TiO}_3$ . The constitution of  $\text{TiO}_3 \cdot 3\text{H}_2\text{O}$  is therefore

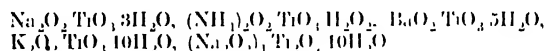


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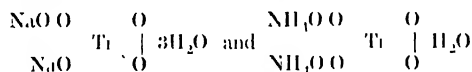


the titanium being in neither case more than quadrivalent.

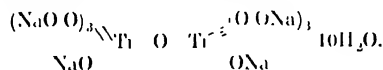
Mehkoff and Pissarjewski<sup>2</sup> have prepared a number of salts of pertitanic acid with metallic superoxides by adding well-cooled hydrogen peroxide to  $\text{TiO}_3$  aq. followed by sufficient alkali to make a clear solution. The salts are then precipitated by alcohol. The following compounds have thus been obtained:



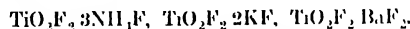
The constitution of the first two salts is represented thus:



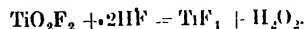
For the last and similar salts Mehkoff and Pissarjewski assume the titanium to be more than quadrivalent, formulating  $(\text{Na}_2\text{O}_2)_4 \cdot \text{Ti}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  as



The *fluoroxypertitanates*, to which reference has been made above, are formed when alkali or alkaline earth fluoride is added to a titanous acid solution containing hydrogen peroxide<sup>3</sup>. The following are examples of these crystalline salts:



They are derivatives of pertitanic acid, in which an atom of oxygen has been replaced by two of fluorine; and are decomposed by hydrofluoric acid thus:



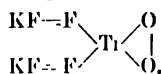
<sup>1</sup> Levy, *Compt. rend.*, 1889, 108, 294

<sup>2</sup> Mehkoff and Pissarjewski, *Zeitsch. anorg. Chem.*, 1899, 19, 413

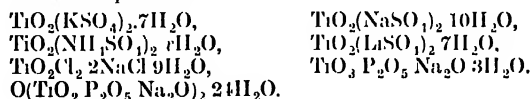
<sup>3</sup> Mehkoff and Pissarjewski, *ibid.*, 1898, 31, 678, 953

<sup>4</sup> Piccini, *Compt. rend.*, 1884, 97, 1064, *Gazzetta*, 1887, 17, 479

The constitution of  $\text{TiO}_2\text{F}_2 \cdot 2\text{KF}$  may be thus represented :



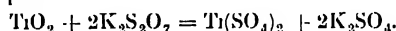
Mazzucchelli and Pantanelli<sup>1</sup> have prepared the following inorganic salts of titanium peroxide:



#### DETECTION AND ESTIMATION OF TITANIUM

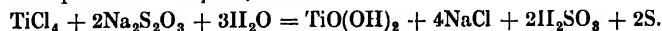
**Detection.**—Titanium is detected in the dry way by the borax or phosphate bead reaction. The bead is not coloured when heated in the outer flame, but in the inner flame shows a yellow colour while hot, and the characteristic violet colour of titanous compounds when cold. The violet colour appears more quickly when a particle of zinc or tin is introduced as a reducing agent. If a small quantity of an iron salt is fused into the titanium bead a red colour is produced in the inner flame. Titanium compounds do not colour the Bunsen flame, but the arc or spark spectrum of this element contains a large number of lines, chiefly in the blue and green.<sup>2</sup>

The titanium present in minerals such as rutile is best brought into solution by fusion with potassium pyrosulphate, when the following reaction takes place :



The fused mass can then be dissolved in cold water. Fusion with sodium carbonate produces sodium metatitanate, insoluble in water, but soluble in acids.

From a titanic solution, the hydroxide,  $\text{Ti}(\text{OH})_4$ , easily soluble in acids, is precipitated by potassium hydroxide in the cold. From the hot solution alkali precipitates less soluble  $\text{TiO}(\text{OH})_2$ . Alkali acetates on boiling cause the precipitation of  $\text{TiO}(\text{OH})_2$  from titanium tetrachloride solution, owing to hydrolysis. Moreover, all titanic salts are hydrolysed when their dilute solutions are boiled; consequently titanium can be separated from aluminium, iron, and chromium by fusion with potassium pyrosulphate,  $\text{K}_2\text{S}_2\text{O}_7$ , dissolving the melt in much cold water and then heating to boiling. Tartaric and citric acids prevent this hydrolysis by the formation of complex salts. Boiling with sodium thiosulphate causes a similar hydrolysis, the thiosulphuric acid formed decomposing with separation of sulphur, thus :



This reaction also serves to separate titanium from iron. Potassium ferrocyanide gives a brown precipitate in slightly acid titanic solutions.

Hydrogen peroxide, when added to a slightly acid solution of a titanic salt, produces a yellow or orange-red colour<sup>3</sup> according to concen-

<sup>1</sup> Mazzucchelli and Pantanelli, *Atti R. Accad. Lincei*, 1909, [v], 18, i, 608.

<sup>2</sup> *Vide p. 234*

<sup>3</sup> Schönc, *Deutsch. Poly J.*, 1873, 210, 317.

tration, owing to the formation of  $TiO_3$ . This is a very delicate reaction for titanium, but vanadic acid gives a similar colour with hydrogen peroxide.

When a solution of a titanic compound in hydrochloric acid is reduced by tin or zinc a violet solution of titanium trichloride is produced which yields a violet precipitate, turning white by oxidation. The violet solution becomes pink on dilution. This is also a delicate colour reaction for titanium. Quadrivalent titanium in moderately dilute solution gives with dihydroxyacetic acid a brilliant orange colour; trivalent titanium gives a dull yellowish brown colour, changed to orange by oxidation.<sup>1</sup>

Titanic oxide is distinguished and separated from silica by heating it with a mixture of hydrofluoric and sulphuric acids. Under these conditions the silica is changed into gaseous silicon tetrafluoride, and is thus eliminated, whilst titanic oxide remains. Indeed, titanium tetrafluoride is quantitatively changed into titanic oxide by evaporation with sulphuric acid.

**Estimation.**—Titanium is estimated gravimetrically in the form of its dioxide,  $TiO_2$ . This is precipitated in the hydrated form by adding ammonia to a titanic solution, or by the hydrolysis of the acetate<sup>2</sup> or sulphate, as explained above.

It may also be estimated colorimetrically, by means of the hydrogen peroxide reaction<sup>3</sup>; this is a method suitable for the determination of small quantities of the element occurring in rocks. The titanium is brought into solution as sulphate by fusion with potassium pyrosulphate,  $K_2S_2O_7$ , and extraction with water; then to a suitably diluted volume of this solution, in presence of free sulphuric acid, hydrogen peroxide is added, and the colour produced is matched with standard titanic sulphate solution. Hydrofluoric acid interferes with this reaction, but small quantities of iron do not; chrome, molybde, and vanadic acids must, however, be absent. A solution of thymol in concentrated sulphuric acid is a more delicate colorimetric reagent for titanium than hydrogen peroxide.<sup>4</sup>

Lastly, titanium may be estimated volumetrically by reducing its acid solution to the trivalent condition by means of zinc, and titrating with standard permanganate solution, with standard ferric chloride solution in presence of potassium thiocyanate,<sup>5</sup> or with standard methylene blue.<sup>6</sup>

<sup>1</sup> Fenton, *Trans. Chem. Soc.*, 1908, 93, 1061; *Ber.*, 1910, 43, 267.

<sup>2</sup> Baerheav and Isham, *J. Amer. Chem. Soc.*, 1910, 32, 957.

<sup>3</sup> Weller, *Ber.*, 1882, 15, 2593.

<sup>4</sup> Lenher and Crawford, *J. Amer. Chem. Soc.*, 1913, 35, 138.

<sup>5</sup> Knecht and Hibbert, *Ber.*, 1903, 36, 1519.

<sup>6</sup> Hibbert, *J. Soc. Chem. Ind.*, 1909, 28, 189; Neumann and Murphy, *Zeitsch. angew. Chem.*, 1913, 26, 613.



## CHAPTER V

### ZIRCONIUM AND ITS COMPOUNDS

#### ZIRCONIUM

Symbol, Zr. Atomic weight, 90.6 (O = 16)

**Occurrence.** The chief zirconium mineral is *zircon* or *hyacinth*, which is the orthosilicate  $ZrSiO_4$ ; it is a common accessory constituent of igneous rocks, such as granite, syenite, diorite, etc., and also occurs in granular limestone. It forms tetragonal crystals, which are frequently brown, but may be colourless, red, yellow, green, blue, etc. Its density is 4.6 to 4.8 and hardness 7.5 on Moh's scale. Colourless and smoky zircon is called *jargon*, and this was thought by Sorby<sup>1</sup> to contain a new element owing to its peculiar absorption spectrum, until it was shown that the observed lines were due to an oxide of uranium. Zircon occurs chiefly in Ceylon, the Urals, the Isle of Harris, Greenland, Australia, and near Green River, North Carolina. *Baddelyte*,<sup>2</sup> which occurs in Ceylon and Brazil, consists of zirconia,  $ZrO_2$ , together with traces of other oxides,<sup>3</sup> and *eudalyte*, *catapleite*, and *zircon-pyroxene* are silicates containing zirconia. Zirconium also occurs in a number of uncommon minerals, together with the rare earths, and is widely diffused through various igneous rocks.

**History.**—In 1789, the year of the discovery of titanium, Klaproth<sup>4</sup> isolated from the mineral zircon a new earth which he called *zirconia*, and in 1795<sup>5</sup> he extracted the same substance from the mineral hyacinth, found in Ceylon. Berzelius,<sup>6</sup> in 1818, traced an analogy between zirconia and alumina; Pfaff,<sup>7</sup> in 1820, showed that zircon and rutile are isomorphous; and Stromeyer,<sup>8</sup> in 1822, found zirconia in the mineral eudalyte. The preparation of metallic zirconium and the study of its compounds was carried out by Berzelius<sup>9</sup> in a series of researches between 1824 and 1835. It was alleged by Svanberg,<sup>10</sup> in 1845, that zirconia contains the oxides of three new elements, but this belief subsequently proved to be erroneous.

**Preparation of Metallic Zirconium.** Zirconia, derived from zircon, is the starting-point for the preparation of metallic zirconium and its compounds. The metal was first obtained by Berzelius,<sup>11</sup> in 1824, by heating together potassium zirconiumfluoride and potassium. The

<sup>1</sup> Sorby, *Chem. News*, 1870, 21, 73.

<sup>2</sup> Weiss and Lehmann, *Zeitsch. anorg. Chem.*, 1909, 65, 178.

<sup>3</sup> Wedekind, *Zeitsch. angew. Chem.*, 1908, 21, 2270; *Lier*, 1910, 43, 290.

<sup>4</sup> Klaproth, *Beitr.*, 1789, 1, 203; *Crelle's Annalen*, 1789, 1, 7.

<sup>5</sup> Klaproth, *Beitr.*, 1795, 1, 227.

<sup>6</sup> Berzelius, *Afhandl. Fys. Kem.*, 1818, 5, 86.

<sup>7</sup> Pfaff, *Schweigger's J.*, 1820, 28, 102.

<sup>8</sup> Stromeyer, *Jahresber.*, 1822, 1, 40.

<sup>9</sup> Berzelius, *Pogg. Annalen*, 1824, 4, 117 *et seq.*

<sup>10</sup> Svanberg, *Pogg. Annalen*, 1845, 65, 317.

<sup>11</sup> Berzelius, *Pogg. Annalen*, 1824, 4, 117.

reaction is analogous to that by which he had obtained silicon in the previous year, viz :



Later, the metal was prepared by Troost<sup>1</sup> by passing zirconium tetrachloride vapour over heated sodium or magnesium. Weiss and Neumann<sup>2</sup> obtained the powdered metal by mixing potassium zirconium fluoride with purified sodium, covering the mixture with potassium chloride, compressing it into an iron vessel, and starting the reaction by means of a flame. The product was washed with alcohol and hydrochloric acid. By substituting aluminium for sodium a better product, containing 99.8 per cent. of the metal, was obtained. Lely and Hamburger<sup>3</sup> have prepared the metal by reducing the anhydrous chloride with sodium in a vacuum.

An alternative method of preparing zirconium is to reduce its oxide by another metal or by carbon. Thus Plüpson<sup>4</sup> heated the dioxide with magnesium powder and obtained zirconium as a black, velvety powder; Winkler,<sup>5</sup> however, on passing hydrogen over a heated mixture of zirconia and magnesium obtained the solid hydride  $\text{ZrH}_2$ , mixed with unchanged zirconia. Wedekind,<sup>6</sup> on the other hand, obtained colloidal zirconium, which formed a dark blue suspension in water, together with the nitride  $\text{Zr}_3\text{N}_2$ , by the reaction between zirconia and magnesium in presence of air.

Moissan<sup>7</sup> prepared zirconium by heating the oxide with excess of carbon in an electric furnace and fusing the resulting carbide with excess of zirconia. The temperature of reduction of zirconia by carbon is about  $4100^\circ\text{C}$ .<sup>8</sup>

Lastly, Wedekind<sup>9</sup> has obtained a metallic powder containing 99 per cent. of zirconium by reducing the dioxide with calcium in an evacuated iron vessel. The powder produced was washed successively with water, acetic acid, dilute hydrochloric acid and acetone in absence of air, dried *in vacuo* at  $250^\circ\text{--}300^\circ\text{C}$ , and then heated to  $800^\circ\text{--}1000^\circ\text{C}$ . The metal has been investigated analytically by Wedekind and Lewis.<sup>10</sup>

**Properties of Zirconium.** Amorphous zirconium, prepared by the method of Berzelius, is a coal-black powder which is a bad conductor of electricity. According to Wedekind and Lewis<sup>11</sup> the black, amorphous zirconium of Berzelius is not an individual substance but a gel, which retains water most pertinaciously. The gel has a density of 3.75, but after drying at  $1000^\circ\text{C}$  in a high vacuum its density becomes 5.79. Amorphous zirconium appears to be the colloidal modification of the metal; and the two modifications of zirconium bear to one another the same relation as do amorphous and crystalline silicon. Crystallised zirconium, as prepared by Weiss and Neumann,<sup>12</sup>

<sup>1</sup> Troost, *Compt. rend.*, 1865, 61, 109.

<sup>2</sup> Weiss and Neumann, *Zeitsch. anorg. Chem.*, 1910, 65, 218.

<sup>3</sup> Lely and Hamburger, *Zeitsch. anorg. Chem.*, 1911, 87, 209.

<sup>4</sup> Plüpson, *Compt. rend.*, 1865, 61, 713.

Winkler, *Ber.*, 1891, 24, 888.

<sup>5</sup> Wedekind, *Zeitsch. anorg. Chem.*, 1907, 45, 388.

<sup>7</sup> Moissan, *Compt. rend.*, 1893, 116, 1212. See also *The Electric Furnace* (Arnold, 1904), p. 172.

<sup>8</sup> Greenwood, *Trans. Chem. Soc.*, 1908, 93, 1195.

<sup>9</sup> Wedekind, *Annalen*, 1913, 395, 119.

<sup>10</sup> Wedekind and Lewis, *Trans. Chem. Soc.*, 1909, 95, 456.

<sup>11</sup> Wedekind and Lewis, *Annalen*, 1913, 395, 119.

<sup>12</sup> Weiss and Neumann, *Zeitsch. anorg. Chem.*, 1910, 65, 218.

is white, and resembles cast-iron. It forms broad, monoclinic plates, and has a density of 4.15 (Troost), 4.25 (Moissan), or 6.40 (Weiss and Neumann). It has a hardness of 7-8 on Moh's scale and scratches glass and the ruby; its specific heat is 0.0666<sup>1</sup> or 0.0804 (Weiss and Neumann); it melts at about 1530° C.<sup>2</sup> The arc, spark, and absorption spectra of the metal have been studied by various observers.<sup>3</sup> The most intense lines in the spectrum of zirconium are as follow<sup>4</sup>:

Arc: 3392.14, 3496.38, 3890.19, 3891.53, 3929.71, 3973.63, 4081.10, 4227.94, 4239.19, 4282.36, 4507.32, 4535.90, 4575.69, 4634.20, 4687.99, 4688.63, 4710.23, 4739.68, 4772.50, 4875.80, 6127.64.

Spark: 3392.20, 3438.39, 3496.40, 3556.89, 3698.41, 3757.85, 3836.98, 3958.39, 3991.31, 3999.18, 4140.43, 4209.21, 4380.12, 4443.31, 4494.78, 4497.27.

The most persistent, i.e. the ultimate lines in the spark spectrum, are 3394.8 and 3392.4.<sup>5</sup>

The crystalline metal is very stable in the air, and burns only slowly at a white heat, though more rapidly in the oxy-hydrogen blowpipe flame; when combustion is incomplete the product contains some sesquioxide, Zr<sub>2</sub>O<sub>3</sub>. The amorphous metal burns more readily. The heat of combustion of 1 gram is 1958.7 calories (Weiss and Neumann). When heated to dull redness in chlorine or hydrogen chloride the metal yields the tetrachloride, and it combines with hydrogen at a red heat to form the solid dihydride ZrH<sub>2</sub>.

Zirconium is but slowly attacked when heated with hydrochloric, nitric, or sulphuric acid, but is rapidly oxidised by aqua regia. Hydrofluoric acid is the best solvent for this metal, the cold dilute acid easily dissolving it; caustic alkalis also dissolve zirconium with evolution of hydrogen. Zirconium preparations sometimes show radioactivity, owing probably to the presence of thorium as an impurity.<sup>6</sup>

#### ATOMIC WEIGHT OF ZIRCONIUM

That the atomic weight of zirconium is approximately 90 is evident from a consideration of its specific heat, and of the isomorphism of its compounds with those of tin, silicon, and lead; and, finally, from a study of the Periodic Table.<sup>7</sup>

Various attempts have been made to determine with accuracy the atomic weight of zirconium. Berzelius<sup>8</sup> in 1825, by igniting the neutral sulphate Zr(SO<sub>4</sub>)<sub>2</sub>, obtained the following value for the ratio



<sup>1</sup> Mörser and Dana, *Annalen*, 1873, 169, 388.

<sup>2</sup> Vide Wedekind, *Annalen*, 1912, 395, 164.

<sup>3</sup> Thälen, *Ann. Chim. Phys.*, 1868, [iv], 18, 228; Troost and Hautefeuille, *Compt. rend.*, 1871, 73, 503; Exner and Haschek, *Sitzungsber. K. Akad. Wiss. Wien*, 1898, KI 11A, 07, 813; Lockyer, *Phil. Trans.*, 1881, 173; Rowland and Harrison, *Astrophys. J.*, 1898, 7, 273, 373; Bachem, *Zeit. Wiss. Photochem.*, 1910, 8, 316; Soret, *Jahresber.*, 1875, 219. See also *B.A. Report*, 1908, 119.

<sup>4</sup> Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

<sup>5</sup> Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1907 8, II, 270.

<sup>6</sup> Gockel, *Chem. Zeit.*, 1909, 33, 1121.

<sup>7</sup> The arguments are precisely the same as those set forth under titanium, p. 235.

<sup>8</sup> Berzelius, *Pogg. Annalen*, 1825, 4, 126.

# ZIRCONIUM AND ITS COMPOUNDS

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whence

$$\text{Zr} = 89.16.^1$$

Hermann<sup>2</sup> in 1844 analysed the tetrachloride  $\text{ZrCl}_4$ , and the basic chloride  $2\text{ZrOCl}_2 \cdot 9\text{H}_2\text{O}$ , the mean of his results yielding the value 89.56 for the atomic weight of zirconium.<sup>3</sup>

More important and accurate were the results of Marignac,<sup>4</sup> published in 1860. This investigator analysed potassium zirconium fluoride,  $\text{K}_2\text{ZrF}_6$ , and obtained the following values for the ratios,

$\text{ZrO}_2 : \text{K}_2\text{ZrF}_6$	0.13200 : 1, whence Zr = 90.03
$\text{K}_2\text{SO}_4 : \text{K}_2\text{ZrF}_6$	0.61365 : 1, „ Zr = 91.54
$\text{ZrO}_2 : \text{K}_2\text{SO}_4$	0.70396 : 1, „ Zr = 90.68.

Assuming equality of accuracy for each of these values, the mean atomic weight of zirconium is 90.75, a result closely approximating to that accepted at the present time.

The above results are now, however, of purely historic interest. The most accurate researches are those of Weibull<sup>5</sup> in 1881, and particularly those of Bailey<sup>6</sup> in 1890 and Venable<sup>7</sup> in 1898.

Weibull ignited the sulphate and selenate of zirconium, obtaining values for the ratios  $\text{ZrO}_2 : \text{Zr}(\text{SO}_4)_2$  and  $\text{ZrO}_2 : \text{Zr}(\text{SeO}_4)_2$ . Bailey similarly ignited the sulphate, but in a double crucible to avoid the loss of traces of the light zirconia which in an ordinary crucible are apt to be carried away mechanically. He thus obtained eight highly concordant values for the ratio  $\text{ZrO}_2 : \text{Zr}(\text{SO}_4)_2$ . Venable prepared the pure basic chloride,  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  by crystallisation from hot hydrochloric acid, and dried it in a stream of hydrogen chloride at  $100^\circ$  to  $125^\circ$  C. Solution in water, followed by evaporation to dryness and subsequent prolonged ignition, converted the salt into the dioxide, thus enabling the ratio  $\text{ZrO}_2 : \text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  to be calculated.

The results of these investigators are given in the following table:

Authority	Ratio Determined	No. of Experiments	Mean Atomic Weight of Zirconium.
Weibull	$\text{ZrO}_2 : \text{Zr}(\text{SO}_4)_2 = 0.13150 : 1$	7	89.54
	$\text{ZrO}_2 : \text{Zr}(\text{SeO}_4)_2 = 0.32558 : 1$	5	90.79
Bailey	$\text{ZrO}_2 : \text{Zr}(\text{SO}_4)_2 = 0.13372 : 1$	8	90.65
Venable	$\text{ZrO}_2 : \text{ZrOCl}_2 \cdot 3\text{H}_2\text{O} = 0.52986 : 1$	10	90.81

<sup>1</sup> This and the succeeding values for the atomic weight of zirconium are not the figures given by the investigators in the original memoirs, but have been calculated from their experimental results, using the modern values for the fundamental atomic weights, namely, O = 16.000, S = 32.065, H = 1.00762, Cl = 35.457, K = 39.100; F = 19.015, and Se = 79.176.

<sup>2</sup> Hermann, *J. prakt. Chem.*, 1844, 31, 77.

<sup>3</sup> See Clarke, *A Recalculation of the Atomic Weights*, Smithsonian Collections, Washington, vol. liv, No. 3, 1910, p. 287.

<sup>4</sup> Marignac, *Ann. Chim. Phys.*, 1860 [m], 60, 270, *Œuvres Complètes*, 1860, n, 15.

<sup>5</sup> Weibull, *Lund Arskrift*, 1881-1882, vol. xvm.

<sup>6</sup> Bailey, *Proc. Roy. Soc.*, 1890, 46, 74.

<sup>7</sup> Venable, *J. Amer. Chem. Soc.*, 1898, 20, 119.

Assuming that the mean values for the atomic weight of zirconium, as given in the last column of the table, are of equal importance, the general mean becomes  $Zr = 90.15$ . But this is unsatisfactory on account of the wide discrepancy between the two values found by Wedgill. The results of Bailey and Venable appear to be the most reliable, the mean of these being  $Zr = 90.73$ . Nevertheless the figure accepted by the International Committee on Atomic Weights for 1917 is  $Zr = 90.6$ ; a value that evidently needs revision.

### COMPOUNDS OF ZIRCONIUM

With the exception of the dihydride and sesquioxide, zirconium is quadrivalent in all its known compounds. In this respect it resembles thorium rather than titanium. The characteristic zirconiumfluorides connect zirconium with silicon, titanium, and tin; the existence of a stable nitrate shows the superior metallic properties of this metal. The chief compounds are here tabulated.

Hydride	$ZrH_2$ (solid)	Superoxides	$Zr_2O_5$ , $ZrO_3$
Halides	$ZrF_4$ , $K_2ZrF_6$ , and other complex fluorides, $ZrCl_4$ , addition compounds with $NH_3$ , etc.	Sulphide	Composition unknown.
	$ZrOCl_2$ , $ZrBr_4$ , $ZrOBr_2$ , $ZrI_4$ , $ZrOI_2$	Oxysulphide	$ZrOS$ .
		Sulphate	$Zr(SO_4) \cdot 4H_2O$ , complex sulphates.
Oxides and	$Zr_2O_3$	Nitrides	$Zr_3N_2$ , $Zr_2N_3$ , $Zr_3$
Hydroxides	$ZrO_2$ , $ZrO_2 \cdot H_2O$ , various zirconates.	Nitrate	$Zr(NO_3)_4 \cdot 5H_2O$
		Carbide	$ZrC$ .
		Silicide	$ZrSi_2$ .
		Silicate	$ZrSiO_4$ .
		Boride	$Zr_3B_4$ .

**Zirconium Hydride,  $ZrH_2$ .**—This hydride does not belong to the category which includes the tetrahydrides of carbon, silicon, and germanium; for these are gaseous hydrides, whilst zirconium hydride is solid, like the hydrides of the alkali and alkaline earth metals. Zirconium hydride was obtained by Winkler,<sup>1</sup> mixed with unchanged zirconia, by passing hydrogen over a heated mixture of zirconia and magnesium powder; by Weiss and Neumann,<sup>2</sup> as a grey solid, when hydrogen is passed over red-hot zirconium; and by Wedekind<sup>3</sup> by heating the powdered metal to  $700^\circ C$ . in hydrogen at a pressure of 1.5 atmosphere. The hydride burns in air to the sesquioxide; its dissociation-pressure up to  $1100^\circ C$ . has been measured by Wedekind.<sup>3</sup>

### ZIRCONIUM AND THE HALOGENS

In accordance with the almost unexceptional quadrivalency of zirconium, only the tetrahalides  $ZrF_4$ ,  $ZrCl_4$ ,  $ZrBr_4$ ,  $ZrI_4$  are known, together with some oxyhalides, double or complex halides, and addition compounds.

<sup>1</sup> Winkler, *Ber.*, 1891, 24, 888

<sup>2</sup> Weiss and Neumann, *Zeitsch. anorg. Chem.*, 1910, 65, 248

<sup>3</sup> Wedekind, *Annalen*, 1913, 305, 149

**Zirconium Fluoride,  $ZrF_4$ ,** is formed when the dioxide is gently heated with twice its weight of ammonium difluoride, and can also be obtained by the action of anhydrous hydrofluoric acid on the tetrachloride<sup>1</sup>. It sublimes in small, highly refractive prisms having a density of 1.333, 110 c.c. of cold water dissolve 1.388 grams of  $ZrF_4$ , and at 50° C. hydrolysis causes the separation of the hydroxide from the solution. On evaporating a hydrofluoric acid solution of the fluoride, trichine tablets of the hydrate  $ZrF_4 \cdot 3H_2O$  crystallise out. This zirconium fluoride possesses some distinctly saline properties. It combines with liquid ammonia to form the compound  $5ZrF_4 \cdot 2NH_3$  (Wolter).

**Zirconium Double or Complex Fluorides.** When potassium fluoride is added to an excess of zirconium fluoride solution a crystalline precipitate of the compound  $K_2ZrF_6$  is obtained. This substance is potassium zirconium fluoride, to which there correspond isomorphous silicifluorides, titanifluorides, and stannifluorides.

Potassium zirconium fluoride is also formed by fusing zircon with potassium hydrogen fluoride. It crystallises from hot water in rhombic prisms, its solubilities at various temperatures being as follow:

Temperature " C . . . . .	2°	15	19°	100°
Grams of $K_2ZrF_6$ in . . . . .				
100 grams of $H_2O$ . . . . .	0.78	1.11	1.70	25.0

By varying the proportions between potassium fluoride and zirconium fluoride the composition of the product may be altered. Thus by pouring a solution of zirconium hydroxide into a concentrated solution of potassium fluoride the salt  $K_3ZrF_7$  or  $K_2ZrF_6 \cdot KF$  is obtained, which crystallises in regular octahedra; on recrystallisation from hot water, however,  $K_2ZrF_6$  separates. When, on the other hand, excess of zirconium fluoride is employed the salt  $KZrF_5 \cdot H_2O$  is formed in monoclinic crystals.

Cesium resembles potassium in forming the stable zirconium fluoride  $Cs_2ZrF_6$ , which can be recrystallised. By varying the proportions between the two components, however,  $CsZrF_5 \cdot H_2O$  or  $CsF \cdot ZrF_4 \cdot H_2O$  and  $2CsF \cdot 3ZrF_4 \cdot 2H_2O$  can be obtained, the former, but not the latter, of these two salts can be recrystallised without decomposition.<sup>2</sup>

The less electropositive sodium<sup>3</sup> does not so readily form the salt  $Na_2ZrF_6$ . This salt is produced when 2 parts of sodium fluoride are added to 11 of zirconium fluoride, but cannot be recrystallised. The salt  $5NaF \cdot 2ZrF_4$ , originally produced by Mangnag,<sup>4</sup> is formed under very wide conditions.

Besides these compounds, ammonium, lithium, and thallium form double salts with zirconium fluoride, as well as the bivalent metals Mg, Zn, Cd, Mn, Ni, and Cu.

**Zirconium Chloride,  $ZrCl_4$ ,** is formed in a variety of ways, which are characteristic of the manner of formation of non-metallic rather than metallic chlorides. Thus it is produced (i) by the action of chlorine on a red-hot mixture of zircon or zirconia and charcoal<sup>5</sup>; in the former

<sup>1</sup> Wolter, *Chem. Zeit.* 1908, 32, 606.

<sup>2</sup> Wells and Foote, *Zeitsch. anorg. Chem.*, 1895, 10, 131.

<sup>3</sup> Wells and Foote, *Amer. J. Sci.*, 1897, 3, 166.

<sup>4</sup> Mangnag, *Ann. Chim. Phys.*, 1860 [m], 60, 257.

<sup>5</sup> Wohler, *Pogg. Annalen*, 1839, 48, 91. Melliss, *Annalen*, 1870, 153, 328; Hinzberg, *Annalen*, 1887, 239, 253.

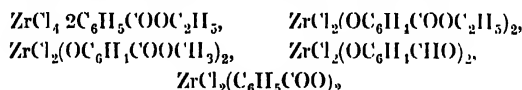
case zirconium tetrachloride is mixed with silicon tetrachloride derived from the silica of the mineral; (ii) by the action of chlorine or hydrogen-chloride gas on the heated metal,<sup>1</sup> when the chloride is obtained as a white, crystalline sublimate; (iii) by the action of chlorine on the carbide,  $\text{ZrC}$ ,<sup>2</sup> at  $300^\circ \text{C}$ .; (iv) by heating the oxide with phosphorus pentachloride in a sealed tube at  $190^\circ$ ;<sup>3</sup> (v) by heating the oxychloride,  $\text{ZrOCl}_2$ , to  $110^\circ \text{C}$ . in a stream of hydrogen chloride.<sup>4</sup> According to Lely and Hamburger,<sup>5</sup> however, zirconium chloride is best prepared by the action of chlorine and carbon tetrachloride on the oxide at  $800^\circ \text{C}$ .; and Bourion<sup>6</sup> has found that the pure chloride is rapidly obtained by passing the vapour of sulphur monochloride over heated thorium.

Zirconium chloride is a white, crystalline solid which fumes in moist air and reacts vigorously with water, forming the oxychloride  $\text{ZrOCl}_2$  which remains in solution. Zirconium chloride forms no crystallohydrate with water, but sublimes when heated, yielding a vapour whose density at  $440^\circ \text{C}$ . is 8.15 (air = 1)<sup>7</sup> or 117.4 ( $\text{H} = 1$ ) (theory for  $\text{ZrCl}_4$  requires 116.2); it may apparently be recrystallised from hydrochloric acid, but the product probably contains some oxychloride.

**Addition Compounds of Zirconium Chloride.** Like other metatelluric chlorides, zirconium tetrachloride forms various addition compounds with ammonia, phosphorus pentachloride, etc.

According to Matthews,<sup>8</sup> the solid tetrachloride combines at ordinary temperature with 2 molecules of ammonia, at higher temperature with 4 molecules, and in ethereal solution yields with ammonia the compound  $\text{ZrCl}_4 \cdot 8\text{NH}_3$ . Stahler and Denk,<sup>9</sup> however, obtained  $\text{ZrCl}_4 \cdot 8\text{NH}_3$  by passing ammonia over zirconium tetrachloride at atmospheric temperature as long as increase in weight occurred. The product was a loose white powder, which easily lost ammonia, and with water produced zirconium hydroxide and ammonium chloride. At a higher temperature the product corresponded approximately to  $\text{ZrCl}_4 \cdot \text{NH}_3$ .

With phosphorus pentachloride the complex  $2\text{ZrCl}_4 \cdot \text{PCl}_5$ ,<sup>10</sup> is formed as a white mass melting at  $240^\circ \text{C}$ . and boiling at  $325^\circ \text{C}$ . The following addition and substitution organic compounds are known<sup>11</sup>:



*Sodium Zirconichloride*,  $\text{Na}_2\text{ZrCl}_6$ , appears to be formed<sup>12</sup> when zirconium chloride is sublimed over fused sodium chloride; and *pyridine* and *quinoline* compounds of this type,  $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ZrCl}_6$  and  $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{ZrCl}_6$ , have been prepared.<sup>13</sup>

<sup>1</sup> Berzelius, *Pogg. Annalen*, 1824, 4, 117; Troost, *Compt. rend.*, 1865, 61, 109.

<sup>2</sup> Wedekind, *Zeitsch. anorg. Chem.*, 1902, 33, 81.

<sup>3</sup> E. F. Smith and Harris, *J. Amer. Chem. Soc.*, 1895, 17, 654.

<sup>4</sup> Venable, *J. Amer. Chem. Soc.*, 1891, 16, 469; *Trans. Chem. Soc.*, 1895, 67, 812.

<sup>5</sup> Lely and Hamburger, *Zeitsch. anorg. Chem.*, 1914, 87, 209.

<sup>6</sup> Bourion, *Ann. Chim. Phys.*, 1910, [viii], 20, 547, 21, 49.

<sup>7</sup> Deville and Troost, *Compt. rend.*, 1857, 45, 821.

<sup>8</sup> Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815.

<sup>9</sup> Stahler and Denk, *Ber.*, 1905, 38, 2611.

<sup>10</sup> Paykull, *Ber.*, 1873, 6, 1467.

<sup>11</sup> Rosenheim and Hertzmann, *Ber.*, 1907, 40, 810.

<sup>12</sup> Paykull, *loc. cit.*

<sup>13</sup> Rosenheim and Frank, *Ber.*, 1905, 38, 812.

**Zirconium Oxychlorides.**—Although zirconium chloride dissolves in water, hydrolysis takes place, the solution becomes acid, and the oxychloride,  $\text{ZrOCl}_2$ , is formed in solution; whilst a solution of zirconium hydroxide in hydrochloric acid deposits on evaporation tetragonal crystals of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .<sup>1</sup> When this compound is heated to 100° C. in a stream of hydrogen chloride  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  is formed, and when it is recrystallised from concentrated hydrochloric acid  $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$  separates.<sup>2</sup> According to Chauvenet<sup>3</sup>  $\text{ZrOCl}_2$  forms hydrates with 2, 3, 5, 6, and 8  $\text{H}_2\text{O}$ . The oxychloride  $\text{Zr}_2\text{OCl}_6$  is formed when the tetrachloride is heated in a current of oxygen,<sup>4</sup> and  $\text{Zr}_2\text{O}_2\text{Cl}_2$  when an alcoholic solution of  $\text{ZrOCl}_2$  is precipitated with ether.<sup>5</sup> Chauvenet,<sup>6</sup> however, maintains that the only oxychloride besides  $\text{ZrOCl}_2$  is  $\text{Zr}_2\text{O}_2\text{Cl}_2$ , which exists in the anhydrous and mono- and tri-hydrated forms. When a solution of zirconium oxychloride is dialysed colloidal zirconium hydroxide results.

**Zirconium Bromide,  $\text{ZrBr}_4$ ,** resembles the chloride in its manner of formation and properties. It is formed by passing bromine vapour with carbon dioxide gas over a heated mixture of zirconia<sup>7</sup> and carbon, or over red-hot zirconium or its carbide.<sup>8</sup> It is a white, crystalline powder which dissolves in water, forming the oxybromide  $\text{ZrOBr}_2$ ; it forms with ammonia gas at 16° C. the compound  $\text{ZrBr}_4 \cdot 10\text{NH}_3$  (Stahler and Denk), and absorbs ammonia in ethereal solution, forming  $\text{ZrBr}_4 \cdot (\text{NH}_3)_9$ . The bromide also combines with ethylamine, aniline, and pyridine, and forms the pyridinium salt  $(\text{C}_5\text{H}_5\text{NH})_2\text{ZrBr}_6$ .<sup>10</sup>

**Zirconium Oxybromides** resemble the oxychlorides.<sup>11</sup> By the evaporation over sulphuric acid of an aqueous solution of the tetrabromide crystals of  $\text{ZrOBr}_2 \cdot 8\text{H}_2\text{O}$ <sup>12</sup> are formed, and when these are heated to 100°–120° C. in a current of hydrogen bromide  $\text{ZrOBr}_2 \cdot \text{H}_2\text{O}$  results; whilst from a solution of titanium hydroxide in hydrobromic acid the compounds  $\text{Zr}(\text{OH})_3\text{Br} \cdot 2\text{H}_2\text{O}$  and  $\text{Zr}(\text{OH})_3\text{Br} \cdot \text{H}_2\text{O}$  can be obtained.

**Zirconium Iodide,  $\text{ZrI}_4$ ,** was prepared in an impure state by Dennis and Spencer<sup>13</sup> by passing hydrogen iodide gas over zirconium heated to redness; and Stahler and Denk<sup>14</sup> obtained the impure iodide as a rust-coloured sublimate by the same method, the metal or the carbide being employed, and freed it from iodine by shaking it with benzene.

Zirconium iodide is a brown powder which fumes in the air and reacts vigorously with water and alcohol; it combines with ether to form  $\text{ZrI}_4 \cdot 4(\text{C}_2\text{H}_5)_2\text{O}$ , and with ammonia to form  $\text{ZrI}_4 \cdot 8\text{NH}_3$ .

**Zirconium Oxy-iodide,  $\text{ZrOI}_2 \cdot 8\text{H}_2\text{O}$ ,** was obtained by Venable and Baskerville<sup>15</sup> by dissolving zirconium hydroxide in hydriodic acid,

<sup>1</sup> Weibull, *Ber.*, 1887, 20, 1394.

<sup>2</sup> Venable and Baskerville, *J. Amer. Chem. Soc.*, 1898, 20, 321.

<sup>3</sup> Chauvenet, *Compt. rend.*, 1912, 154, 821.

<sup>4</sup> Troost and Hautefeuille, *Compt. rend.*, 1871, 73, 563.

<sup>5</sup> Erdmann, *J. prakt. Chem.* 1875, [n], 11, 219.

<sup>6</sup> Chauvenet, *Compt. rend.*, 1912, 154, 1234.

<sup>7</sup> Melliss, *Bull. Soc. chim.*, 1870, 14, 204.

<sup>8</sup> Stahler and Denk, *Ber.*, 1905, 38, 812.

<sup>9</sup> Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815, 839, 843.

<sup>10</sup> Rosenheim and Frank, *Ber.*, 1905, 38, 812.

<sup>11</sup> Melliss, *Bull. Soc. chim.*, 1870, 14, 204; Weibull, *Ber.*, 1887, 20, 1394.

<sup>12</sup> Rosenheim and Frank, *Ber.*, 1907, 40, 803.

<sup>13</sup> Dennis and Spencer, *J. Amer. Chem. Soc.*, 1896, 18, 473.

<sup>14</sup> Stahler and Denk, *Ber.*, 1904, 37, 1137; 1905, 38, 2611.

<sup>15</sup> Venable and Baskerville, *J. Amer. Chem. Soc.*, 1898, 20, 321.



and by Stahler and Denk<sup>1</sup> by evaporating a solution of zirconium tetraiodide in water. It forms colourless crystals.

### ZIRCONIUM AND THE OXYGEN GROUP

**Oxides of Zirconium.** It has already been seen that zirconium is usually quadrivalent. Nevertheless the sesquioxide  $Zr_2O_3$  exists, though probably not the monoxide  $ZrO$ . Winkler<sup>2</sup> believed that the monoxide  $ZrO$  is formed when zirconia is heated with magnesium in a current of hydrogen, and this opinion was supported by the work of Dennis and Spencer<sup>3</sup>; Wedekind,<sup>4</sup> however, failed to obtain a lower oxide by the reduction of zirconia with magnesium; the existence of the monoxide must therefore be considered doubtful.

**Zirconium Sesquioxide,  $Zr_2O_3$ .** was obtained by Weiss and Neumann<sup>5</sup> by the combustion of the hydride  $ZrH_2$ . It formed a green powder which on ignition in the air passed slowly into the dioxide.

**Zirconium Dioxide (Zirconia),  $ZrO_2$ .** It has already been stated that zirconia occurs in various minerals, both free and combined with silica and other oxides. Zircon,  $ZrSiO_4$ , is the chief source of zirconia and other compounds of zirconium; and in order to prepare this mineral for chemical treatment it is ignited and quickly plunged into cold water; by this means it is rendered pulverisable. The powdered mineral may then be treated in various ways, the chief of which are:

- (i) Fusion with alkali carbonate or hydroxide.
- (ii) Fusion with potassium hydrogen fluoride.
- (iii) Fusion with potassium hydrogen sulphate.
- (iv) Reduction with carbon in the electric furnace.

(i) *Fusion with Alkali Carbonate or Hydroxide*--When powdered zircon is fused with alkali carbonate or hydroxide and the melt is treated with water, alkali zirconate remains as a crystalline powder. After washing, this powder is dissolved in dilute hydrochloric or sulphuric acid, and from the solution thus obtained hydrated zirconia is precipitated by ammonia.

(ii) *Fusion with Potassium Hydrogen Fluoride.* The powdered zircon is intimately mixed with about four times its weight of potassium hydrogen fluoride,<sup>6</sup> and gently ignited in a platinum crucible till it is freed from water. The platinum crucible is then placed inside a covered Hessian crucible and the whole is heated in a wind-furnace for two hours. The melt, after cooling, is boiled with dilute hydrofluoric acid, and the silicon is thus eliminated as almost insoluble potassium silicofluoride, which is filtered off. From the filtrate potassium zirconiofluoride crystallises on cooling; this salt is recrystallised and then decomposed with strong sulphuric acid. From a solution of the zirconium sulphate thus formed, hydrated zirconia is precipitated by ammonia.<sup>7</sup>

<sup>1</sup> Stahler and Denk, *Ber.*, 1904, 37, 1137, 1905, 38, 2611

<sup>2</sup> Winkler, *Ber.*, 1890, 23, 2661

<sup>3</sup> Dennis and Spencer, *J. Amer. Chem. Soc.*, 1896, 18, 673

<sup>4</sup> Wedekind, *Zeitsch. anorg. Chem.*, 1905, 45, 385

<sup>5</sup> Weiss and Neumann, *Zeitsch. anorg. Chem.*, 1909, 65, 218

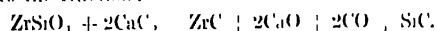
<sup>6</sup> Maignac, *Ann. Chim. Phys.*, 1860, [iii], 60, 257

<sup>7</sup> Homberger, *Annalen*, 1876, 181, 232

(iii) *Fusion with Potassium Hydrogen Sulphate*.—When zircon is fused with potassium hydrogen sulphate and the mass is boiled with water containing sulphuric acid a residue of basic zirconium sulphate,  $\frac{1}{2}\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 11\text{H}_2\text{O}$ , is obtained.<sup>1</sup> This is then decomposed by fusion with caustic soda, so that after washing with water a residue of zirconia remains, which is purified by being dissolved in hot concentrated sulphuric acid and reprecipitated, after dilution, by ammonia.

(iv) *Reduction with Carbon in the Electric Furnace*. Troost<sup>2</sup> endeavoured to eliminate silica from zircon by mixing the latter with carbon, compressing the mixture into a cylinder and heating it in the electric arc surrounded with an atmosphere of carbon dioxide. Although most of the silica was reduced and vapourised, about 1 per cent. remained in the residue. Moissan and Lengfeld<sup>3</sup> heated a mixture of zircon and sugar-charcoal in the electric furnace; the silicon was volatilised and the zirconium formed a carbide containing a very small amount of silicon. This carbide was decomposed at a dull red heat by chlorine and the resulting chlorides were boiled with concentrated hydrochloric acid, whence zirconium chloride separated almost pure. This was then decomposed in solution by ammonia, and pure hydrated zirconia obtained, free from iron and silicon.

A modification of this process consists in the addition of lime,<sup>4</sup> whereby calcium carbide is formed and becomes the reducing agent according to the reaction:



According to Wedekind<sup>5</sup> it is best to dissolve the zirconium carbide in aqua regia and then add tartaric acid and hydrogen peroxide, which precipitates the peroxide.

Zirconia may be obtained in a pure state by the ignition of hydrated zirconia, or of the nitrate, sulphate, or oxalate of the metal. Produced thus it is a fine white powder of density 5.189<sup>6</sup> or 5.1824.<sup>7</sup> When zirconia is fused with borax and the borax is extracted with sulphuric acid the zirconia is obtained in tetragonal prisms, of density 5.71,<sup>8</sup> and isomorphous with rutile and cassiterite, but not with thorium. Crystallised zirconia is also produced when the powdered oxide is heated with hydrogen chloride gas under pressure.<sup>9</sup> Zirconia fuses in the electric furnace; its density at 15° C. after fusion is 5.75 (Lehmann). The coefficient of linear expansion of zirconia is 0.00000081, that of quartz being 0.0000007. The temperature to which it has been heated has much influence on the solubility of zirconia in acids, for, like alumina and some other oxides, it undergoes polymerisation on ignition. Thus after slight ignition zirconia is easily soluble in mineral acids, but after strong ignition it dissolves only in concentrated sulphuric and hydrofluoric acids.

<sup>1</sup> Franz, *Ber.*, 1870, 3, 58.

<sup>2</sup> Troost, *Compt. rend.*, 1893, 116, 1128.

<sup>3</sup> Moissan and Lengfeld, *Compt. rend.*, 1896, 122, 651.

<sup>4</sup> Renaux, *Contribution à l'étude de la Zirconie*, Thèse, Paris-Vincennes, 1900.

<sup>5</sup> Wedekind, *Zeitsch. anorg. Chem.*, 1902, 33, 81.

<sup>6</sup> Venable and Beldon, *J. Amer. Chem. Soc.*, 1898, 20, 273.

<sup>7</sup> Lehmann, *Untersuchungen über das Zirkonoxyl und seine Verwendung*, München, 1908.

<sup>8</sup> Nordenskiöld, *Pogg. Annalen*, 1861, 114, 612.

<sup>9</sup> Hautefeuille and Percy, *Compt. rend.*, 1890, 110, 1038.

It was observed by Berzelius, as early as 1825, that zirconia, when strongly heated, emits a bright light; and this oxide, when made into rods or plates, has been employed as a substitute for lime in the Drummond light. It was also used by Auer von Welsbach as a constituent of the earlier mantles for incandescent gas light, and by Nernst in the preparation of the rods for his electric glow-lamp. Its power of withstanding high temperature and chemical reagents, and its very low coefficient of expansion make zirconia a suitable material from which to manufacture crucibles. In a crucible made of zirconia mixed with 10 per cent. of magnesia, platinum and quartz can be melted.

**Zirconium Hydroxide, Zirconic Acid.**—Hydrated zirconia, precipitated from an acid solution by ammonia or caustic alkali, contains an indefinite amount of water; it is slightly soluble in water, and appears to be feebly alkaline, since it colours yellow turmeric paper brown. Its solubility in acids depends on the conditions of its precipitation. When precipitated cold it is easily soluble in dilute acids; when precipitated hot, or washed with hot water, it can be dissolved only in concentrated acid. In these properties hydrated zirconia resembles hydrated alumina. When precipitated zirconia is heated to 100° C. it attains to the composition  $\text{ZrO}_2 \cdot \text{H}_2\text{O}$ . This product is called zirconic acid. A less hydrated form of zirconia, known as metazirconic acid, is obtained by boiling zirconium oxychloride with water as long as chloride is abstracted and drying the product at 100° C.; it has the composition  $3\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ . Metazirconic and zirconic acids are supposed to be related to one another as stannic and metastannic acids are related.<sup>1</sup> According to van Bemmelen,<sup>2</sup> however, zirconia forms no true hydroxide, these products being the colloidal oxide, containing accidental amounts of water.

**Zirconates.**—Zirconium hydroxide, if such a compound can be said to exist, is an amphoteric hydroxide forming salts both with strong acids and strong bases. Zirconates of the alkali and other metals are known, but they are produced by fusion rather than in solution; precipitated zirconia adsorbs a certain amount of alkali added in excess, but does not definitely combine with it.

Sodium Metazirconate,  $\text{Na}_2\text{ZrO}_3$ , is formed when zirconia and sodium carbonate are fused together<sup>3</sup> in equivalent proportions. It is a crystalline mass which is decomposed by water. By using excess of sodium carbonate and heating the mixture to whiteness the orthozirconate  $\text{Na}_4\text{ZrO}_4$  is produced. Lithium forms the zirconates  $\text{Li}_2\text{ZrO}_3$ <sup>4</sup> and  $\text{Li}_2\text{Zr}_2\text{O}_5$ , and calcium, strontium, barium, and magnesium the metazirconates  $\text{M}''\text{ZrO}_3$ .

**Zirconium Peroxide and the Perzirconates.**—Cleve<sup>5</sup> prepared a hydrated zirconium peroxide, supposed to be  $\text{ZrO}_3 \cdot n\text{H}_2\text{O}$ , by precipitating with ammonia a mixture of zirconium sulphate solution and hydrogen peroxide; and Bailey<sup>6</sup> obtained a gelatinous precipitate which he believed to be hydrated  $\text{Zr}_2\text{O}_5$ , by adding hydrogen peroxide to a neutral solution of zirconium sulphate.

<sup>1</sup> Ruer, *Zeitsch. anorg. Chem.*, 1905, 43, 285.

<sup>2</sup> Van Bemmelen, *Zeitsch. anorg. Chem.*, 1905, 45, 83. 1906, 49, 125.

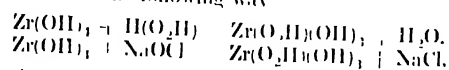
<sup>3</sup> Hottelahl, *Compt. rend.*, 1865, 61, 175, 213.

<sup>4</sup> Ouviard, *Compt. rend.*, 1891, 112, 1444, 113, 80.

<sup>5</sup> Cleve, *Bull. Soc. chim.*, 1885, 43, 57.

<sup>6</sup> Bailey, *Trans. Chem. Soc.*, 1886, 49, 140, 481. and 1889, 58, 705.

More recently Pissarjewski<sup>1</sup> has investigated the action of hydrogen peroxide and of sodium hypochlorite on hydrated zirconia, and represents the reactions in the following way



It is noteworthy that hydrogen peroxide and sodium hypochlorite, which usually differ widely in oxidising action, are here represented as yielding identical oxidation products. From this it is argued that the product is really a derivative of  $\text{ZrO}_2$  and not the double compound  $\text{Zr(OH)}_4 \cdot \text{H}_2\text{O}_2$ .

No precipitate is obtained on adding hydrogen peroxide to a zirconium salt solution in presence of sodium or potassium hydroxide, because the alkali perzirconates are soluble salts. Salts having the formula  $\text{Na}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$  and  $\text{K}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$  respectively are obtained by dissolving zirconium peroxide in alkaline hydrogen peroxide solution and precipitating with alcohol.

**Zirconium Sulphide and Oxy-sulphide.** According to Berzelius<sup>2</sup> and Paykull,<sup>3</sup> zirconium disulphide,  $\text{ZrS}_2$ , is formed when zirconium is heated in sulphur vapour. The metal employed by these workers was, however, highly impure, and the nature of the product obtained uncertain. Frémy made an unsuccessful attempt to prepare a sulphide by heating zirconia in an atmosphere of carbon disulphide; but Hauser,<sup>4</sup> after heating zirconium sulphate in a current of dry air at  $380-400^\circ\text{C}$ , raised it to a red heat in a stream of hydrogen sulphide, and thus obtained zirconium oxy-sulphide,  $\text{ZrOS}$ , as a bright yellow powder which easily takes fire spontaneously in the air.

**Zirconium Sulphates.**—Anhydrous zirconium sulphate,  $\text{Zr(SO}_4)_2$ , is obtained by dissolving the hydrated oxide in concentrated sulphuric acid, evaporating, and carefully igniting the residue. Too strong ignition decomposes the salt and converts it into oxide.<sup>5</sup> The anhydrous sulphate dissolves in much water with great evolution of heat,<sup>7</sup> owing to the formation of the hydrate  $\text{Zr(SO}_4)_2 \cdot 11\text{H}_2\text{O}$ , which separates in rhombic crystals from a solution containing sulphuric acid. From a dilute solution the basic salt  $(\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 15\text{H}_2\text{O})$  gradually separates,<sup>8</sup> and is sufficiently definite in composition for atomic weight determination; whilst from a concentrated solution near the boiling-point the salt  $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$  crystallises.<sup>9</sup> The precipitate formed by adding alcohol to zirconium sulphate solution varies with temperature and concentration.<sup>10</sup> From strongly acid solutions the acid salt  $\text{Zr(SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  separates,<sup>9</sup> in prisms which deliquesce in air, forming  $\text{Zr(SO}_4)_2 \cdot 11\text{H}_2\text{O}$ , the monohydrate  $\text{Zr(SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  is also known.

Ruer<sup>11</sup> has observed that a solution of normal zirconium sulphate does not give the same reactions with oxalic acid and ammonium oxalate

<sup>1</sup> Pissarjewski, *Zeitsch. anorg. Chem.*, 1902, 31, 359.

<sup>2</sup> Berzelius, *Pogg. Annalen*, 1824, 4, 117.

<sup>3</sup> Paykull, *Bull. Soc. chim.*, 1873, [n], 20.

<sup>4</sup> Hauser, *Zeitsch. anorg. Chem.*, 1907, 53, 74.

<sup>5</sup> Berzelius, *Pogg. Annalen*, 1824, 4, 117.

<sup>6</sup> Bailev, *Proc. Roy. Soc.*, 1889, 46, 71.

<sup>7</sup> Hauser, *Zeitsch. anorg. Chem.*, 1905, 45, 185.

<sup>8</sup> Hauser, *ibid.*, see also Hauser and Herzfeld, *ibid.*, 1910, 67, 399.

<sup>9</sup> Hauser, *ibid.*, 1907, 54, 196.

<sup>10</sup> Hauser, *J. prakt. Chem.*, 1907, [n], 76, 363.

<sup>11</sup> Ruer, *Zeitsch. anorg. Chem.*, 1904, 42, 87.

that a solution of the chloride gives. He therefore assumes that this solution contains zirconium in a complex anion, thus  $\text{H}_2(\text{ZrOSO}_4\text{SO}_4)$ , to which complex sodium and ammonium salts  $\text{M}'_2(\text{ZrOSO}_4\text{SO}_4)$  correspond. The constitution of hydrated crystallised zirconium sulphate is accordingly represented thus:  $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ . This view is not accepted by Hauser<sup>1</sup>; but Rosenheim and Frank<sup>2</sup> write the formula in question  $\text{ZrO}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , thus representing it as zirconylsulphuric acid; and, moreover, have obtained the following complex sulphates:

$\text{Zr}_2\text{O}_3(\text{SO}_4\text{K})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Zr}_2\text{O}_3(\text{SO}_4\text{Rb})_2 \cdot 15\text{H}_2\text{O}$ ,  $\text{Zr}_2\text{O}_3(\text{SO}_4\text{Cs})_2 \cdot 11\text{H}_2\text{O}$ , as well as  $\text{Zr}(\text{SO}_4\text{K})_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Zr}(\text{SO}_4\text{Na})_3 \cdot 11\text{H}_2\text{O}$ .

**Zirconium Sulphite**,  $\text{Zr}(\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$ , is obtained in crystals when sulphur dioxide is passed into a zirconium salt solution, and the resulting precipitate is dissolved in sulphurous acid and the solution evaporated over sulphuric acid.<sup>3</sup> A basic thiosulphate also appears to exist.

**Zirconium Selenate**,  $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ , forms hexagonal crystals, soluble in water, which lose  $3\text{H}_2\text{O}$  at  $100^\circ\text{C}$ . and become anhydrous at  $120^\circ\text{C}$ .<sup>4</sup>

**Zirconium Selenite**,  $\text{Zr}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$ , exists in microscopic crystals, insoluble in water. An amorphous basic selenite,  $\text{ZrOSeO}_3 \cdot 2\text{H}_2\text{O}$ , is also known.<sup>5</sup>

#### ZIRCONIUM AND THE NITROGEN GROUP

**Zirconium Nitrides.**—Zirconium does not combine with nitrogen so readily as titanium. Three nitrides, however, have been described:  $\text{Zr}_3\text{N}_2$ ,  $\text{Zr}_2\text{N}_3$ , and  $\text{Zr}_3\text{N}_4$ , but Wedekind<sup>6</sup> appears recently to recognise the existence of only one nitride, viz.  $\text{Zr}_3\text{N}_2$ .

$\text{Zr}_3\text{N}_2$  is formed as a red-brass crystalline powder, of density 6.75, when the metal is heated to  $1050^\circ\text{C}$ . in a current of nitrogen or to  $1000^\circ\text{C}$ . in ammonia gas; it is very stable towards oxygen and chlorine, but evolves ammonia when fused with potash.<sup>7</sup>

$\text{Zr}_2\text{N}_3$  and  $\text{Zr}_3\text{N}_4$ .—By heating a mixture of amorphous zirconium with aluminium to a white heat in the air Mallet<sup>8</sup> obtained a product which evolved ammonia when fused with potash; and similar products were obtained by heating the metal or its chloride in ammonia. More definite knowledge was gained later by Matthews,<sup>9</sup> who obtained  $\text{Zr}_3\text{N}_4$  as a grey product by heating  $\text{ZrCl}_4 \cdot 8\text{NH}_3$  in a current of nitrogen; and  $\text{Zr}_2\text{N}_3$ , which was similar in appearance, by heating the tetrachloride in a stream of ammonia. Wedekind<sup>10</sup> also obtained  $\text{Zr}_2\text{N}_3$  in bronze-coloured microscopic crystals by reducing zirconia with magnesium in a loosely covered crucible and washing away the colloidal metal; the same nitride is also formed when the carbide is heated in a current of nitrogen. Both these nitrides are soluble in hydrofluoric acid.

<sup>1</sup> Hauser, *Zeitsch. anorg. chem.*, 1907, 54, 196.

<sup>2</sup> Rosenheim and Frank, *Ber.*, 1905, 38, 812, and 1907, 40, 803.

<sup>3</sup> Venable and Baskerville, *J. Amer. Chem. Soc.*, 1895, 17, 118.

<sup>4</sup> Ditté, *Compt. rend.*, 1887, 104, 172.

<sup>5</sup> Nilson, *Researches on Salts of Selenious Acid* (Upsala, 1875).

<sup>6</sup> Wedekind, *Annalen*, 1913, 395, 149.

<sup>7</sup> Wedekind, *Annalen*, 1912, 395, 177, 1913, 395, 149.

<sup>8</sup> Mallet, *Amer. Jour. Sci.*, 1859, [n], 28, 349.

<sup>9</sup> Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815, 839, 843.

<sup>10</sup> Wedekind, *Zeitsch. anorg. Chem.*, 1905, 45, 385.

**Zirconium Nitrates.**—The salt  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , first described by Paykull,<sup>1</sup> was obtained by Roschmann and Frank<sup>2</sup> in hygroscopic prisms by evaporating a nitric acid solution of zirconium hydroxide over phosphoric oxide and sodium hydroxide. Maell<sup>3</sup> obtained a basic nitrate soluble in water, and Muller<sup>4</sup> in a study of colloidal zirconium hydroxide, formed the opinion that zirconium nitrate and other zirconium salts are not of constant composition, because a solution containing the nitrate loses nitric acid on evaporation, and the product which dissolves in water, yields a slightly opalescent solution containing colloidal zirconia. The question here arises whether, in analogy with the sulphate, zirconium nitrate,  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  should be written as zirconyl-nitric acid,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , but the question cannot be certainly answered. On evaporating a solution of the nitrate at  $75^\circ \text{C}$ , the basic nitrate  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  separates as a white powder, and on mixing the alcoholic solution of this salt with ether the more basic nitrate  $\text{Zr}_2\text{O}_3(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$  is formed.<sup>5</sup>

**Zirconium Phosphates.** Zirconium orthophosphate is formed as a gelatinous precipitate when a phosphatic solution is added to a solution of a zirconium salt. The compound  $\text{ZrO}_2 \cdot \text{P}_2\text{O}_5$  or  $\text{ZrP}_2\text{O}_7$ , zirconium pyrophosphate, is obtained crystalline when zirconia is fused with metaphosphoric acid, and  $2\text{ZrO} \cdot \text{P}_2\text{O}_5$  is formed in cubical or octahedral crystals when hydrated zirconia is heated with syrupy phosphoric acid. Various double phosphates of zirconium and the alkali metals have been prepared by Troost and Onviard<sup>6</sup> by melting zirconium oxide, phosphate, or chloride with an alkali phosphate.

## \* ZIRCONIUM AND THE CARBON GROUP

**Zirconium Carbide,  $\text{ZrC}$ .** Zirconium is stable, titanium in its power of combining with carbon at high temperature. Troost<sup>8</sup> obtained a carbide to which he attributed the formula  $\text{ZrC}$ , by heating zircon with carbon in the electric arc in an atmosphere of carbon dioxide. Moissan and Langfeld<sup>9</sup> produced a carbide, similarly, by heating in an electric furnace a mixture of pure zirconium and near carbon, mixed with oil and made into cylinders, which were placed in a carbon tube. The carbide was grey and metallic-looking, was well crystallised, was hard enough to scratch glass, but not ruby, had the composition  $\text{ZrC}$ , and was not decomposed by water at  $0^\circ \text{C}$  or  $100^\circ \text{C}$ . In this latter respect it differs from thorium carbide, which, like the carbides of more electropositive metals, is decomposed by water with evolution of hydrocarbons. Wedekind<sup>10</sup> has prepared this carbide from natural zirconia by a similar process, has shown that it is an excellent conductor of electricity, and that it is converted into the nitride when heated in a stream of nitrogen.

<sup>1</sup> Paykull, *Ber.*, 1871, 6, 1167.

<sup>2</sup> Roschmann and Frank, *Ber.*, 1907, 40, 804.

<sup>3</sup> Maell, *Zeitsch. anorg. Chem.*, 1903, 37, 252.

<sup>4</sup> Muller, *Zeitsch. anorg. Chem.*, 1907, 52, 316.

<sup>5</sup> Knop, *Annalen*, 1871, 157, 363.

<sup>6</sup> Harbison and Merrett, *Compt. rend.*, 1886, 103, 1017.

<sup>7</sup> Troost and Onviard, *Compt. rend.*, 1886, 102, 1112; 1887, 105, 39, 255.

<sup>8</sup> Troost, *Compt. rend.*, 1893, 116, 1227.

<sup>9</sup> Moissan and Langfeld, *Compt. rend.*, 1896, 122, 673.

<sup>10</sup> Wedekind, *Chem. Zeit.*, 1907, 31, 651.

**Zirconium Carbonates.**—The existence of several carbonates of zirconium serves to emphasise the electropositive character of this element. Berzelius<sup>1</sup> and Hermann<sup>2</sup> obtained hydrated carbonates by precipitation, and Mandl<sup>3</sup> prepared a precipitated carbonate by passing carbon dioxide through a mixture of zirconium nitrate and ammonium carbonate solutions. Chauvenet<sup>4</sup> has reinvestigated the subject and finds that when a zirconium salt is precipitated by sodium carbonate of any concentration the compound  $\text{ZrCO}_3 \cdot \text{ZrO}_2 \cdot 8\text{H}_2\text{O}$  is formed as a gelatinous, microcrystalline mass which becomes  $\text{ZrCO}_3 \cdot \text{ZrO}_2 \cdot 2\text{H}_2\text{O}$  in an exhausted desiccator.  $\text{ZrCO}_3$  may be regarded as an ortho-carbonate or a basic carbonate  $\text{ZrO} \cdot \text{CO}_2$ . When the above salt is heated beyond  $60^\circ \text{C}$ . it loses carbon dioxide and water, forming  $2\text{ZrCO}_3 \cdot 3\text{ZrO}_2 \cdot 3\text{H}_2\text{O}$ , which at  $250^\circ \text{C}$ . yields a product of the composition  $\text{ZrCO}_3 \cdot 3\text{ZrO}_2 \cdot \text{H}_2\text{O}$ , and at  $100^\circ \text{C}$ . is converted into zirconium dioxide. No anhydrous carbonate appears to exist, but when the dehydrated basic carbonate is exposed to a pressure of 30–40 atmospheres of carbon dioxide it is converted into the hydrated ortho-carbonate  $\text{ZrCO}_3 \cdot 2\text{H}_2\text{O}$ .

**Zirconium Organic Compounds.** A basic formate,<sup>5</sup> the normal and basic acetate,<sup>6</sup> the acetylacetonate,<sup>7</sup> and various oxalates and tartrates<sup>8</sup> of zirconium have been prepared, as well as certain organic compounds of zirconium chloride.<sup>9</sup>

**Zirconium Silicide,  $\text{ZrSi}_2$ ,** was obtained by Wedekind<sup>10</sup> by reducing zirconia with excess of crystalline silicon, and by Hönigschmid<sup>11</sup> by means of the Goldschmidt reaction, in which 200 grams of powdered aluminium, 250 grams of sulphur, 180 grams of fine sand, and 15 grams of zirconium or 40 grams of potassium zirconfluoride,  $\text{K}_2\text{ZrF}_6$ , were mixed together in a Hessian crucible, covered with a layer of powdered magnesium, and ignited. The purified product forms small steel-grey crystals of the hardness of felspar and of density 4.88; the powdered substance burns when heated in the air and dissolves in hydrofluoric acid with evolution of hydrogen. Colloidal zirconium silicide has also been obtained by Wedekind.<sup>12</sup>

**Zirconium Silicate,  $\text{ZrSiO}_4$ ,** occurs naturally as the mineral zircon which has already been described; and it has been produced synthetically in various ways, e.g. by heating zirconia<sup>13</sup> or a mixture of zirconia and quartz<sup>14</sup> in a current of silicon tetrafluoride, by heating a mixture of zirconia and silica with lithium molybdate to  $800^\circ \text{C}$ .<sup>15</sup> or a mixture

<sup>1</sup> Berzelius, *Ann. Chim. Phys.*, 1825, 337.

<sup>2</sup> Hermann, *Jahresber.*, 1886, 89, 191.

<sup>3</sup> Mandl, *Zeitsch. anorg. Chem.*, 1903, 37, 252.

<sup>4</sup> Chauvenet, *Bull. Soc. chim.*, 1913, [iv], 13, 454.

<sup>5</sup> Haber, *Monatsh.*, 1898, 18, 687.

<sup>6</sup> Haber, *loc. cit.*; Mandl, *Zeitsch. anorg. Chem.*, 1903, 37, 252; Rosenheim and Hertzmann, *Ber.*, 1907, 40, 810.

<sup>7</sup> Biltz and Cheneb, *Zeitsch. anorg. Chem.*, 1904, 40, 218.

<sup>8</sup> Packull, *Ber.*, 1879, 12, 1749; Mandl, *loc. cit.*; Rosenheim and Frank, *Ber.*, 1907, 40, 803; Venable and Baskerville, *J. Amer. Chem. Soc.*, 1897, 19, 12.

<sup>9</sup> Rosenheim and Hertzmann, *loc. cit.*

<sup>10</sup> Wedekind, *Ber.*, 1902, 35, 3932.

<sup>11</sup> Hönigschmid, *Compt. rend.*, 1906, 143, 224.

<sup>12</sup> Wedekind, *Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 249.

<sup>13</sup> Deville and Caron, *Compt. rend.*, 1858, 46, 764.

<sup>14</sup> Deville, *Compt. rend.*, 1861, 52, 780.

<sup>15</sup> Hautefeuille and Percy, *Compt. rend.*, 1888, 107, 1000.

of gelatinous zirconia and gelatinous silica nearly to redness under pressure.<sup>1</sup>

#### ZIRCONIUM AND BORON

**Zirconium Boride,  $ZrB_2$** , was obtained by Tucker and Moody<sup>2</sup> as a hard, crystalline, difficultly fusible substance by heating together 5 grams of zirconium and 1.1 gram of boron by means of a current of 200 amperes at 6.5 volts. Wedekind<sup>3</sup> also obtained a boride in the reduction of zirconia by boron in the electric furnace.

#### ZIRCONIUM AND VANADIUM, MOLYBDENUM, AND TUNGSTEN

The complex salts  $(ZrCl_4)_2(VO_4)_2 \cdot 2ZrO_2$ ,  $ZrCl_4 \cdot 2Zr(WO_4)_2 \cdot 2ZrO_2$ , and the molybdate  $Zr(MoO_4)_2$  have been prepared.<sup>4</sup>

#### DETECTION AND ESTIMATION OF ZIRCONIUM

Many investigations have been made of the analytical behaviour of zirconium in order to distinguish it from thorium and the metals of the rare earths, and to separate it quantitatively from iron, titanium, and other metals with which it occurs naturally.

**Detection.** Sodium and potassium hydroxides, ammonia, and ammonium sulphide solutions precipitate zirconium hydroxide, which is insoluble in excess of alkali hydroxide and is thus distinguished from the hydroxides of aluminium and glucinum. Ammonium carbonate solution produces a flocculent precipitate of basic carbonate, which is soluble in excess of the reagent but is reprecipitated on boiling.

There are three reactions by which zirconium is distinguished from thorium.

(1) Solution of oxalic acid or of an oxalate precipitates white zirconium oxalate, which is soluble in excess of either reagent. In the case of thorium it is the neutral oxalate alone, and not also free oxalic acid solution which dissolves the precipitated oxalate.

(2) Hydrofluoric acid precipitates thorium but not zirconium, for zirconium fluoride, unlike thorium fluoride, forms a double or complex fluoride with a soluble fluoride added in excess.

(3) From a cold solution of a zirconium salt potassium sulphate gradually precipitates potassium zirconyl sulphate, but from a boiling solution a basic zirconium sulphate insoluble in dilute hydrochloric acid is precipitated. Thorium does not form such an insoluble basic sulphate.

Hydrogen peroxide precipitates zirconium peroxide from neutral or slightly acid solutions of zirconium salts; in presence of alkali there is no precipitation since the alkali perzirconates are soluble in water, and by this means iron can be separated from zirconium.

Sodium thiosulphate precipitates zirconium hydroxide mixed with sulphur. Turmeric paper is coloured reddish brown when moistened with a hydrochloric acid solution of a zirconium salt and then dried.

Zirconia is distinguished from other earths by its infusibility in the oxyhydrogen flame, in which it glows brightly.

<sup>1</sup> Christ schoff, *Jahrb. Miner.*, 1892, n, 232.

<sup>2</sup> Tucker and Moody, *Proc. Chem. Soc.*, 1901, 17, 129.

<sup>3</sup> Wedekind, *Ber.*, 1902, 35, 3929.

<sup>4</sup> Tanatar and Kurovski, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 813.



**Estimation.**—Zirconium is invariably estimated by being converted into the dioxide  $\text{ZrO}_2$ , which is ignited and weighed as such. Compounds of iron and titanium, however, frequently occur together with zirconium, and various methods have been devised to separate the latter metal from the two former metals.

*Separation of Zirconium and Iron.*—Since zirconium is not precipitated by sodium hydroxide in presence of hydrogen peroxide, iron may be quantitatively separated as ferric hydroxide by adding to the mixed solution sodium peroxide dissolved in ice-water; the zirconium can then be estimated in the filtrate.<sup>1</sup>

On the other hand, concentrated hydrogen peroxide precipitates zirconium peroxide from acid solution, and according to Bailey<sup>2</sup> this reaction suffices to separate zirconium from iron and titanium.

Iron can also be quantitatively separated from zirconium and other metals by the use of nitroso- $\beta$ -naphthol.<sup>3</sup> According to Rivet<sup>4</sup> iron may be estimated when obtained as ferric oxide mixed with undecomposable oxides by determining the loss of weight which is caused by reduction in hydrogen; and Gutbier and Huller<sup>5</sup> have applied this method to the estimation of iron and zirconium. According to Daniel and Leberle,<sup>6</sup> however, the method gives variable results according to the proportion of iron present, and the question has been the subject of considerable controversy.<sup>7</sup>

Titanium and zirconium can be separated from iron by passing hydrogen sulphide through a solution of the mixed sulphates to reduce the iron, displacing hydrogen sulphide by sulphur dioxide to prevent oxidation, and adding sodium acetate, ammonium sulphate, sulphurous acid or sodium thiosulphate, all of which precipitate titanium and zirconium, leaving iron in solution.<sup>8</sup>

*Separation of Zirconium and Titanium.*—The following method of estimating zirconium and titanium, when they occur together, as, for example, in rocks, is recommended by Dittrich and Pohl.<sup>9</sup> The precipitated oxides are fused with potassium hydrogen sulphate, and the solution of sulphates thus obtained is reduced with hydrogen sulphide. Tartaric acid is then added, followed by ammonia and ammonium sulphide; thus the iron alone is precipitated. The tartaric acid is removed from the filtrate, and the titanium and zirconium are then precipitated and weighed together. The mixture is subsequently dissolved in potassium persulphate solution, sulphuric acid and hydrogen peroxide are added, and the titanium is then estimated colorimetrically.

An alternative method for separating titanium and zirconium<sup>10</sup> consists in adding a solution containing their nitrates, neutralised with sodium carbonate, to a boiling concentrated solution of ammonium salicylate. The zirconium is precipitated, and all the titanium is in the filtrate.

<sup>1</sup> Giesow and Horkheimer, *Zeitsch. anorg. Chem.*, 1902, 32, 372.

<sup>2</sup> Bailey, *Trans. Chem. Soc.*, 1886, 49, 149, 181.

<sup>3</sup> Knott, *Zeitsch. anorg. Chem.*, 1901, 17, 641, 676.

<sup>4</sup> Rivet, *Ann. Chim. Phys.*, 1870, [vol. 30, 188.

<sup>5</sup> Gutbier and Huller, *Zeitsch. anorg. Chem.*, 1902, 32, 92.

<sup>6</sup> Daniel and Leberle, *Zeitsch. anorg. Chem.*, 1903, 34, 393.

<sup>7</sup> Daniel, Leberle, Gutbier, and Trenkner, *Zeitsch. anorg. Chem.*, 1903, 36, 302; Daniel, *ibid.*, 37, 475; Gutbier, *ibid.*, 1904, 39, 257.

<sup>8</sup> Dittrich and Freund, *Zeitsch. anorg. Chem.*, 1907, 56, 337.

<sup>9</sup> Dittrich and Pohl, *Zeitsch. anorg. Chem.*, 1905, 43, 236.

<sup>10</sup> Dittrich and Freund, *Zeitsch. anorg. Chem.*, 1907, 56, 344.

## CHAPTER VI

### THORIUM AND ITS COMPOUNDS

#### THORIUM

Symbol, Th. Atomic weight, 232.1 (0-16)

**Occurrence.**—Thorium was first discovered in minerals occurring in Scandinavia. The chief of these are *thorite* and its gem-variety *orange*, which are silicates of very complex composition. Thorite contains nearly 60 per cent. of thorium, about 20 per cent. of silica, and smaller quantities of urane, ferric, manganic, copper, magnesium, potassium, sodium, lead, tin, and aluminum oxides. Scandinavian minerals containing smaller quantities of thorium are: *monazite* (phosphate), *gadolinite* (silicate), *citronite* (columbo-tantalate), *samaraskite* (columbo-tantalate), and numerous other minerals in which the trivalent rare earth elements occur in considerable quantities. A mineral richer in thorium than any of the preceding is *thorianite*,<sup>1</sup> which contains about 80 per cent. of thorium associated with the oxides of uranium and the trivalent rare earth elements. This mineral was discovered in Ceylon about 1901, but unfortunately is rather scarce, and therefore does not constitute an important source of thorium. In the earlier years of the man-made gas mantle, that is about 1885, the world-supply of thorium was insufficient to meet the demand.

Subsequent to 1895, however, large quantities of monazite have been discovered, not in the form of the crystalline mineral, but in the form of *monazite sand*. These sands have been produced by the weathering of rocks which originally contained a very small percentage of monazite, and the subsequent washing away of the lighter materials produced. The monazite in the sands is associated with numerous other minerals, from which, however, it may be separated without much difficulty. Monazite is essentially an orthophosphate of the cerium group of rare earth elements, but it almost invariably contains some thorium, probably as phosphate.<sup>2</sup> Deposits of monazite sand occur in various parts of the globe, notably in Brazil and in the native State of Travancore, India. These sands constitute almost the only source of the thorium used in the gas-mantle industry. The composition of Brazilian sand, as concentrated for exportation, varies between the following limits:<sup>3</sup>

<sup>1</sup> Dunstan and Blake, *Proc. Roy. Soc.*, 1905, A, 76, 533; Dunstan and B. M. Jones, *ibid.*, 1906, A, 77, 546.

<sup>2</sup> Kress and Metzger, *J. Amer. Chem. Soc.*, 1909, 31, 610.

<sup>3</sup> This and other information in this section is taken from a lecture on "Thorium and its Compounds," delivered before the Institute of Chemistry by Edmund White, 1912. See also Johnstone, *The Rare Earth Industry* (Grosvenor, Lockwood and Son, Ltd., 1915); Levy, *The Rare Earths* (Arnold, 1914).

ThO <sub>2</sub>	5-7	per cent.	La <sub>2</sub> O <sub>3</sub>	} 20-30 per cent.	Y <sub>2</sub> O <sub>3</sub>	1-5 per cent.
P <sub>2</sub> O <sub>5</sub>	25-30	"	Pr <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	1-4 "
Ce <sub>2</sub> O <sub>3</sub>	25-35	"	Nd <sub>2</sub> O <sub>3</sub>		Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , MnO,	
					CaO, MgO, PbO,	
					SnO <sub>2</sub> , traces.	

Concentrated Travancore sand is considerably richer in thorium than the above. The North American (North and South Carolina, Idaho) deposits of monazite sand are now of little or no commercial value.<sup>1</sup>

Thorium is found in minute quantities in various igneous and sedimentary rocks.<sup>2</sup>

**History.** - In 1817 Berzelius<sup>3</sup> examined the Swedish mineral now known as *gadolinite*, and isolated from it what he believed to be a new earth, the oxide of a metal which he named thorium, after the Scandinavian god Thor. Subsequently, however, Berzelius<sup>4</sup> concluded that his earth was a basic phosphate of yttrium, a metal which had been discovered by Gadolin in 1794. In 1828,<sup>5</sup> however, he prepared from a mineral now known as *thorite*, from the island of Lovon, near Brevig, in Norway, a new earth, rather resembling the former product, which he named thoria. He then showed that the new element resembled zirconium in properties. In 1851 Bergemann<sup>6</sup> announced the discovery of a new metal, which he called donarium, in the mineral *orangeite*, but Damour,<sup>7</sup> Berlin,<sup>8</sup> Delafontaine,<sup>9</sup> and Bergemann<sup>10</sup> himself subsequently showed donarium to be identical with thorium. In 1862 Bahr<sup>11</sup> thought he had discovered, in a mineral from Ronsholm, a new metal which he called wasium, but two years<sup>12</sup> later he showed that wasium was identical with thorium.

Metallic thorium was first obtained by Berzelius<sup>14</sup> in 1828, also by Chydemus<sup>15</sup> in 1861, and in a purer state by Nilson<sup>15</sup> in 1882. From experiments on the fractional distillation of the chloride Baskerville,<sup>16</sup> in 1901, concluded that thorium contains two other elements which he named berzelmium and carolumium. This opinion, however, has not been confirmed.<sup>17</sup>

**Extraction of Thorium Compounds from Monazite Sand and other Minerals.**—The economic value of monazite sand depends on the per-

<sup>1</sup> A fuller account of monazite sand and a selection of analyses of monazite will be found in vol. iv, chap. x.

<sup>2</sup> Blane, *Atto R. Acad. Lincei*, 1909 [v], 18, 1, 241, 289, July, *Phil. Mag.* 1909 [iv], 17, 760, 1910, [vi], 20, 125.

<sup>3</sup> Berzelius, *Affhandl. Fys., Kem. och Min.*, 1817, 5, 76.

<sup>4</sup> Berzelius, *K. Svenska Vet.-Akad. Handl.*, 1, 1821, 315.

<sup>5</sup> Berzelius, *K. Svenska Vet.-Akad. Handl.*, 1, 1829, 1.

<sup>6</sup> Bergemann, *Pogg. Annalen*, 1851, 82, 582.

<sup>7</sup> Damour, *Compt. rend.*, 1852, 34, 685.

<sup>8</sup> Berlin, *Pogg. Annalen*, 1852, 85, 555.

<sup>9</sup> Delafontaine, *Arch. Sci. phys. nat.*, 1863, 18, 343.

<sup>10</sup> Bergemann, *Pogg. Annalen*, 1852, 85, 558.

<sup>11</sup> Bahr, *Pogg. Annalen*, 1862, 119, 572.

<sup>12</sup> Bahr, *Annalen*, 1864, 132, 227.

<sup>13</sup> Berzelius, *Pogg. Annalen*, 1829, 16, 385.

<sup>14</sup> Chydemus, *Pogg. Annalen*, 1861, 119, 13.

<sup>15</sup> Nilson, *Pæ.*, 1882, 15, 2537.

<sup>16</sup> Baskerville, *J. Amer. Chem. Soc.*, 1901, 23, 761, 1904, 26, 922, *ibid.*, 1905, 27, 1414;

also Brauner, *Proc. Chem. Soc.*, 1901, 17, 67.

<sup>17</sup> Meyer and Gumpelz, *Ber.*, 1903, 38, 17, Eberhard, *ibid.*, 826.

centage of thorina it contains; if this falls below 5 per cent. the value of the sand is reduced, if below 1 per cent. it becomes very small. Consequently means are taken to remove foreign matter occurring with the sand—first by means of water, in imitation of tidal action, and secondly, by taking advantage of the different magnetic susceptibilities of monazite and its associated minerals. This concentration of the sand is effected prior to its exportation, and can be carried out so effectively that less than 5 per cent. of foreign matter remains in association with the monazite.

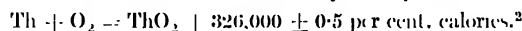
For decomposing the sand it has been proposed to mix it with lime, coke, and a little fluor spar, and to heat the mixture in an electric furnace until phosphorus ceases to be evolved.<sup>1</sup> The usual plan, however, is to decompose it with sulphuric acid. The first step, known as "breaking," consists in heating the sand to about 200° C. with twice its weight of sulphuric acid of 1.81 density until the monazite is completely decomposed. A thick whitish paste is produced, which is gradually stirred into water and the insoluble matter allowed to settle. The solution then contains the sulphates of the various metals, together with the excess of sulphuric acid and the phosphoric acid derived from the monazite. To separate the thorium from this solution advantage is usually taken of the fact that thorium phosphate is less soluble in dilute acid than the phosphates of the other metals that are present. Consequently, by partially neutralising the acid solution a precipitate is obtained rich in thorium phosphate. As a neutralising agent magnesia has numerous advantages over others that might be proposed. This fractional precipitation of the thorium phosphate must be repeated several times before a precipitate is obtained consisting almost entirely of the thorium salt, and a certain proportion of the thorium is inevitably lost in the mother liquors which carry away the bulk of the other rare earth elements.

The subsequent operations are concerned mainly with removing phosphoric acid and the remainder of the trivalent rare earth elements from the thorium. For eliminating phosphoric acid, the crude thorium phosphate may be dissolved in hydrochloric acid and the rare earths precipitated as oxalates by the addition of oxalic acid. Numerous methods have been described for removing the other rare earths still present; these are based upon the following facts: (i) When thorium is precipitated, together with other metals, as basic carbonate by means of sodium carbonate solution, an excess of precipitant redissolves the thorium salt, whereas the carbonates of the cerium metals are almost insoluble in sodium carbonate and those of the yttrium metals (which are present only in very small amount) are but slightly soluble; (ii) thorium oxalate is readily soluble in ammonium oxalate solution, in which the oxalates of the accompanying rare earth elements are practically insoluble; (iii) the hydrated sulphates of thorium and the accompanying rare earth element are comparatively sparingly soluble in water and their relative solubilities are widely different; and (iv) thorium acetate is considerably less soluble in water than the acetates of the other rare earth elements.

The sulphate crystallisation (iii) is widely used. At 15° C. the following hydrates are in equilibrium with their solutions, and their solubilities are as follow:

<sup>1</sup> Baskerville, *J. Ind. Eng. Chem.*, 1912, 4, 821; *Chem. News*, 1912, 106, 271.

of microscopic, hexagonal plates; it had a density of 11.0, whence that of the pure metal was calculated to be 11.10. Von Bolton's metal had a density of 11.32 and, after rolling and heating, 12.16. The specific heat of thorium, according to the mean of six determinations made by Nilson,<sup>1</sup> is 0.02787. The metal burns brilliantly to the oxide when heated in the air, though less easily in the form of ribbon than in powder. Its heat of combustion is given by the equation



It melts at about 1450° C. in a vacuum (von Bolton); von Wartenburg's metal, however, containing about 2 per cent. of carbide melted at 1700° C. In colour, softness, and ductility thorium resembles platinum. It combines on heating, with the halogens, sulphur, hydrogen, and nitrogen; it dissolves with difficulty in hydrochloric acid, and its reaction with nitric acid soon comes to a standstill, owing to the metal becoming passive; it dissolves rapidly in aqua regia, but alkalis are without action upon it.<sup>3</sup> Colloidal thorium has been obtained by Wedekind and Baumhauer.<sup>4</sup> The radioactivity of thorium will be dealt with in a special section.

The most *intense* lines in the arc and spark spectra of thorium are as follow<sup>5</sup>:

Arc: 3188.33, 3511.76, 3741.36, 4019.29, 4382.02, 4391.29, 4752.60, 4863.38, 4919.99, 5017.39, 5049.93, 5989.22, 6162.83.

Spark: 2411.38, 3221.10, 3290.73, 3300.63, 3313.87, 3507.72, 3538.90, 4019.30, 4382.10, 4391.30.

The most *persistent* spark lines, which should be looked for when seeking traces of thorium, are as follow<sup>6</sup>:

2519.7, 2551.8, 2555.3, 2870.5, 3290.7, 4382.1, 4391.3.

#### ATOMIC WEIGHT OF THORIUM

It was assumed by Berzelius, who first investigated thorium and its compounds, that thoria is analogous to magnesia, and should therefore be represented by the formula ThO, the metal having an atomic weight of approximately 116. The formula ThO<sub>2</sub> was first adopted by Delafontaine in 1863, on account of the isomorphism of thoria with tinstone and rutile, and of certain complex salts of thorium with similar salts of zirconium. That the atomic weight of thorium is about 232 is proved by the following facts:

(i) The radioactivity of thorium shows it to be an element of high atomic weight.

(ii) The specific heat of thorium is 0.02787. Assuming a mean atomic heat of 6.4, the atomic weight by Dulong and Petit's Law is about 230.

(iii) The transparency of thorium to X-rays is in accordance with a value for the atomic weight equal to four times the equivalent weight.<sup>7</sup>

<sup>1</sup> Nilson, *Ber.*, 1883, 16, 153, *Compt. rend.*, 1883, 96, 316.

<sup>2</sup> Von Wartenburg, *Zetsch. Elektrochem.*, 1909, 15, 866.

<sup>3</sup> Moissan and Haugschmid, *Ann. Chim. Phys.*, 1905 [viii], 8, 482.

<sup>4</sup> Wedekind and Baumhauer, *Zetsch. Chem. Ind. Kolb.*, 1909, 5, 191.

<sup>5</sup> Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

<sup>6</sup> Leonard, *Sci. Proc. Roy. Dubl. Soc.*, 1908, 11, 270.

<sup>7</sup> Benoist and Copaux, *Compt. rend.*, 1914, 158, 689.

(iv) Not only is thoria isomorphous with cassiterite and rutile, but the complex nitrates of thorium and cerium of the type  $\text{MgRv}(\text{NO}_3)_6 \cdot 8\text{H}_2\text{O}$ , and thorium and uranous sulphates  $\text{Rv}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ , are also respectively isomorphous. Hence by analysing these compounds and applying Mitscherlich's Law of Isomorphism an atomic weight of 232 is arrived at.

(v) An appropriate position is found for thorium in the periodic system if its atomic weight is 232.

Numerous attempts have been made to determine accurately the atomic weight of thorium.

Berzelius<sup>1</sup> converted the oxide into the sulphate and then precipitated the latter with barium, obtaining the mean value of 238.9, calculated according to modern atomic weight values. Chydenius<sup>2</sup> analysed the simple and complex sulphates, and also the acetate, formate, and oxalate. The mean atomic weight calculated from his values is 236.83.

Delafontaine<sup>3</sup> estimated the thorium in the hydrated sulphate  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ , and obtained the value 232.31.

The foregoing results are now merely of historical interest. Cleve<sup>4</sup> analysed the anhydrous sulphate as well as the oxalate. Nilson<sup>5</sup> estimated the thorium in  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$  and also in the anhydrous sulphate. Kruss and Nilson<sup>6</sup> likewise determined the ratio  $\text{ThO} : 2\text{SO}_3$ . Estimations have also been made by Hermann,<sup>7</sup> Brauner,<sup>8</sup> Urbain,<sup>9</sup> W. Biltz,<sup>10</sup> and by Meyer and Gumpertz.<sup>11</sup>

The more important of these researches are given in the following table:

Authority	Ratio	Atomic Weight of Thorium <sup>12</sup>
Cleve (1874)	$\text{Th}(\text{SO}_4)_2 : \text{ThO}_2$ 100 : 62.423	234.01
	$\text{ThO}_2 : \text{HClO}_4$ 151.444 : 100	233.98
Nilson (1882)	$\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O} : \text{ThO}_2$ 100 : 45.091	232.61
	$\text{Th}(\text{SO}_4)_2 : \text{HClO}_4$ 100 : 62.297	232.51 <sup>11</sup>
Kruss and Nilson (1887)	$\text{Th}(\text{SO}_4)_2 : \text{ThO}_2$ 100 : 62.297	232.59
		232.49 <sup>11</sup>
Meyer and Gumpertz (1905)	$\text{Th}(\text{SO}_4)_2 : \text{ThO}_2$ 100 : 62.288	232.45

<sup>1</sup> Berzelius, *Pogg. Annalen*, 1820, 10, 298.

<sup>2</sup> Chydenius, *Pogg. Annalen*, 1861, 119, 44.

<sup>3</sup> Delafontaine, *Arch. Sci. phys. nat.*, 1863, [iv], 18, 343.

<sup>4</sup> Cleve, *Ekong K. Svenska Vet.-Akad. Handlingar*, 1871, 2, No. 6.

<sup>5</sup> Nilson, *Ber.*, 1882, 15, 2519.

<sup>6</sup> Kruss and Nilson, *Ber.*, 1887, 20, 1665.

<sup>7</sup> Hermann, *J. prakt. Chem.*, 1884, 93, 111.

<sup>8</sup> Brauner, *Zeitsch. anorg. Chem.*, 1903, 35, 207. *Proc. Chem. Soc.*, 1898, 191, 68, and 1901, 235, 67. *Trans. Chem. Soc.*, 1898, 73, 951.

<sup>9</sup> Urbain, *Ann. Chim. Phys.*, 1900, [vi], 10, 224.

<sup>10</sup> W. Biltz, *Annalen*, 1904, 331, 450. <sup>11</sup> R. J. Meyer and Gumpertz, *Ber.*, 1905, 38, 817.

<sup>12</sup> Based upon the following values for the fundamental atomic weights: O = 16.000, S = 32.065, H = 1.00752.

<sup>13</sup> Recalculated by Brauner and corrected to vacuum weighings. See *Handbuch der*

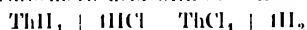
The figure adopted by the International Atomic Weights Committee from 1900 to 1908 was 232.5. In 1909 the value was changed to 232.12, and at the present time (1917) the figure accepted is **232.4**. This value is in need of revision, for it is almost impossible to be certain that thorium (which figures in all the above ratios) was weighed free from moisture and adsorbed gases.<sup>1</sup>

### COMPOUNDS OF THORIUM

Thorium appears to be strictly quadrivalent in all its compounds; and though it is by no means a powerful metal, on the whole, base-producing predominate over acid-producing properties. The following is an epitome of the chief compounds of thorium:

Hydride	ThH <sub>4</sub>
Fluoride	ThF <sub>4</sub> ; also ThOF <sub>2</sub> , double fluorides, silicofluoride.
Chloride	ThCl <sub>4</sub> ; ThCl <sub>4</sub> ·8H <sub>2</sub> O, oxychloride, addition compounds, complex chlorides
Bromide	ThBr <sub>4</sub> ; hydrate, oxybromide, addition compounds.
Iodide	ThI <sub>4</sub> , hydrate; oxyiodide.
Chlorate, bromate, iodate, perchlorate	
Dioxide	ThO <sub>2</sub> ; meta-oxide; hydroxide, Th(OH) <sub>4</sub> .
Superoxides	Th <sub>2</sub> O <sub>7</sub> ; ThO <sub>3</sub>
Sulphide	ThS <sub>2</sub> , ThOS
Sulphite	Th(SO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O, complex sulphites
Sulphate	Th(SO <sub>4</sub> ) <sub>2</sub> ; various hydrates, double or complex sulphates.
Selenite	Th(SeO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O; acid selenites
Selenate	Th(SeO <sub>4</sub> ) <sub>2</sub> ·9H <sub>2</sub> O.
Nitride	Th <sub>3</sub> N <sub>4</sub>
Nitrate	Th(NO <sub>3</sub> ) <sub>4</sub> ·12H <sub>2</sub> O, complex nitrates.
Carbide	ThC <sub>2</sub>
Carbonates	Basic and complex salts. Various salts of organic acids
Silicide	ThSi <sub>4</sub>
Silicates	ThSiO <sub>4</sub> ; ThSi <sub>2</sub> O <sub>6</sub> .
Borides	ThB <sub>4</sub> , ThB <sub>6</sub> .

**Thorium Hydride, ThH<sub>4</sub>** It was observed by Winkler<sup>2</sup> that a heated mixture of thorium and magnesium absorbs hydrogen, and it was supposed that the greyish black product contained ThH<sub>2</sub>. Matignon,<sup>3</sup> however, obtained the hydride ThH<sub>4</sub> by the combination of the metal with hydrogen at a red heat. It is a solid not acted on by water but dissolved by hydrochloric acid with evolution of hydrogen, thus:



The formula was established by the measurement of the hydrogen evolved from a known weight of hydride. The hydride dissociates

*anorganischen Chemie*, Meyer and Auerbach, 1909, vol. iii, and using the following antecedent data: O = 16.000, S = 32.06, H = 1.007.

<sup>1</sup> Holmes and Lawson (*Phil. Mag.*, 1911, [viii], 28, 823) announce that Hongschmid has redetermined the atomic weight of thorium, and found Th = 232.2. Details are at present lacking.

<sup>2</sup> Winkler, *Ber.*, 1891, 24, 873.

<sup>3</sup> Matignon, *Compt. rend.*, 1900, 131, 891.

when heated, and at 390°C. dissociation is complete under atmospheric pressure.<sup>1</sup>

#### THORIUM AND THE HALOGENS—HALIDES

**Thorium Fluoride**,  $\text{ThF}_4$ . Anhydrous thorium fluoride,  $\text{ThF}_4$ , is obtained as a white, amorphous powder by passing hydrogen fluoride over the chloride or bromide, heated to 350–400°C.<sup>2</sup>

The hydrated fluoride  $\text{ThF}_4 \cdot 10\text{H}_2\text{O}$  is formed as a gelatinous precipitate, passing into a heavy white powder, when hydrofluoric acid is added to a solution of a thorium salt. Unlike zirconium fluoride, thorium fluoride is insoluble in hydrofluoric acid; this difference furnishes a means for the quantitative separation of the two metals.<sup>3</sup> When strongly ignited in air the fluoride leaves a residue of thorium.<sup>4</sup>

**Thorium Oxyfluoride**,  $\text{ThOF}_2$ , is formed when the precipitated hydrated fluoride is heated to 800°C. in a stream of anhydrous hydrofluoric acid.

**Thorium Double Fluorides**. Thorium fluoride appears to form several double salts with alkali fluorides, but since these are all insoluble in water their chemical identity is somewhat doubtful.

**Potassium Thoriofluoride**,  $\text{K}_2\text{ThF}_6 \cdot 10\text{H}_2\text{O}$ , is formed as an amorphous, insoluble powder when freshly precipitated thorium hydroxide is boiled with a concentrated solution of potassium fluoride containing hydrofluoric acid.<sup>5</sup> The precipitate obtained by adding thorium chloride to potassium hydrogen fluoride solution is possibly  $\text{KTh}_2\text{F}_{10} \cdot 6\text{H}_2\text{O}$  whilst with neutral potassium fluoride the product is  $\text{KThF}_6 \cdot 10\text{H}_2\text{O}$ . When thorium fluoride and potassium fluoride are heated together and the mass is extracted with water  $\text{KThF}_6$  remains, and when redissolved rubidium fluoride is added to a thorium salt solution  $\text{RbThF}_6 \cdot 3\text{H}_2\text{O}$  is precipitated.<sup>6</sup> The amorphous and insoluble natures of these compounds differentiate them from other double or complex fluorides of the fourth group.

**Thorium Chloride**,  $\text{ThCl}_4$ , was prepared by Berzelius<sup>7</sup> by the chlorination of a mixture of thorina and carbon heated in a porcelain tube, by Smith and Harris<sup>8</sup> through the interaction of thorina and phosphorus pentachloride, and by Kruss and Nilson<sup>9</sup> by heating the metal to redness in a stream of hydrogen chloride gas. Thorium chloride has been obtained by Rosenheim, Sauter, and Davidsohn,<sup>10</sup> together with two hydroxychlorides, by the interaction of freshly precipitated thorium hydroxide and alcoholic hydrogen chloride. Thus the two crystalline products  $\text{Th}(\text{OH})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  and  $\text{Th}(\text{OH})_2\text{Cl} \cdot 7\text{H}_2\text{O}$  separated under different conditions, and from the mother liquor  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$  and  $\text{ThCl}_4 \cdot 9\text{H}_2\text{O}$  were obtained in crystals. Matignon and Bourion<sup>11</sup> prepared anhydrous thorium chloride in large prismatic needles by passing a mixture of chlorine and the vapour of sulphur monochloride ( $\text{S}_2\text{Cl}_2$ )

<sup>1</sup> Matignon and Delapme, *Ann. Chim. Phys.*, 1907, [sixt] 10, 130.

<sup>2</sup> Chauvenet, *Compt. rend.*, 1908, 146, 973.

<sup>3</sup> Delafontaine, *Chem. News*, 1897, 75, 230.

<sup>4</sup> Ghydenus, *Progr. Analyt.*, 1861, 119, 13.

<sup>5</sup> Ghydenus, *Progr. Analyt.*, 1861, 119, 13.

<sup>6</sup> Rosenheim, Sauter, and Davidsohn, *Zets. physikal. Chem.*, 1903, 35, 121.

<sup>7</sup> Berzelius, *Progr. Analyt.*, 1829, 16, 38.

<sup>8</sup> E. F. Smith and Harris, *J. Amer. Chem. Soc.*, 1895, 17, 651.

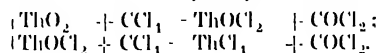
<sup>9</sup> Kruss and Nilson, *Ber.*, 1887, 20, 1665; *Zets. physikal. Chem.*, 1887, 1, 301.

<sup>10</sup> Rosenheim, Sauter, and Davidsohn, *loc. cit.*

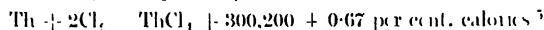
<sup>11</sup> Matignon and Bourion, *Compt. rend.*, 1904, 138, 631.



over heated thoria, and Bourion has found that the vapour of sulphur monochloride alone is sufficient<sup>1</sup>; whilst Moissan and Martensen<sup>2</sup> obtained thorium chloride in colourless crystals by the action of chlorine on thorium carbide at high temperature; and, lastly, Matignon and Delépine<sup>3</sup> have prepared it by passing a current of carbon monoxide and chlorine over thoria heated strongly in a porcelain tube, or by the action of carbon tetrachloride vapour on thoria heated below the melting-point of the chloride, the principal reactions being:



According to Chauvenet,<sup>4</sup> however, thorium chloride is most conveniently prepared, free from oxychloride, by heating the dioxide in a current of carbonyl chloride. The heat of formation of thorium tetrachloride is given by the equation



Thorium chloride forms colourless crystals of density 4.59; it sublimates at 720–750° C., forming shining tablets, and melts at 820° C. It is deliquescent and dissolves readily in water, whence it crystallises as the hydrate  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ . When this hydrate is dried at ordinary temperature and pressure it yields  $\text{ThCl}_4 \cdot 7\text{H}_2\text{O}$ , and this salt, when heated to 50° C. in a current of dry hydrogen, passes into  $\text{ThCl}_4 \cdot 4\text{H}_2\text{O}$ , which at 100° C. yields  $\text{ThCl}_4 \cdot 2\text{H}_2\text{O}$ . Above 100° C. basic chlorides are formed. The heats of solution of the anhydrous salt and the different hydrates are:  $\text{ThCl}_4$ , 56,700 calories;  $\text{ThCl}_4 \cdot 2\text{H}_2\text{O}$ , 11,080 calories;  $\text{ThCl}_4 \cdot 4\text{H}_2\text{O}$ , 26,230 calories;  $\text{ThCl}_4 \cdot 7\text{H}_2\text{O}$ , 11,700 calories;  $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ , 11,150 calories.<sup>6</sup>

The hydrated chloride is readily prepared by dissolving the hydroxide in concentrated hydrochloric acid and saturating the cold solution with hydrogen chloride gas. The salt separates out as a beautiful white crystalline precipitate, and the yield is practically quantitative if an equal volume of ether be added while the gas is being passed into the solution.<sup>7</sup>

**Thorium Oxychloride**,  $\text{ThOCl}_2$ , which is the first product of the interaction of thoria and carbon tetrachloride, may be isolated in the form of small colourless needles, which dissolve in water without decomposition.<sup>8</sup> It is also formed when  $\text{ThCl}_4 \cdot 7\text{H}_2\text{O}$  is heated to 250° C. Its heat of solution in water is 28,150 calories at 13° C. (Chauvenet). Crystalline-hydrates with 3, 5, and 6 molecules of water are known.

**Addition Compounds of Thorium Chloride; Complex Thorium Chlorides.**—Thorium chloride forms compounds with 1, 6, 7, 12, and 18 molecules of ammonia, of which  $\text{ThCl}_4 \cdot 4\text{NH}_3$  is the only compound stable above 120° C.; when heated it forms successively  $\text{Th}(\text{NH}_2)_4$  and  $\text{Th}(\text{NH}_2)_2$ .<sup>9</sup> Thorium chloride also forms addition compounds with

<sup>1</sup> Bourion, *Ann. Chim. Phys.*, 1910, [viii], 20, 547, 21, 49.

<sup>2</sup> Moissan and Martensen, *Compt. rend.*, 1905, 140, 1510.

<sup>3</sup> Matignon and Delépine, *Ann. Chim. Phys.*, 1907, [viii], 10, 130.

<sup>4</sup> Chauvenet, *Compt. rend.*, 1908, 147, 1016.

<sup>5</sup> Von Wartenberg, *Zeitsch. Elektrochem.*, 1909, 15, 896.

<sup>6</sup> Chauvenet, *Compt. rend.*, 1909, 149, 289.

<sup>7</sup> Private communication from H. F. V. Liddle, of Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815, 839.

<sup>8</sup> Matignon and Delépine, *Ann. Chim. Phys.*, 1907, [viii], 10, 130.

<sup>9</sup> Chauvenet, *Compt. rend.*, 1910, 157, 387, *Ann. Chim. Phys.*, 1911, [viii], 23, 275.

various organic bases, and with ethyl alcohol, acetone, and various aldehydes.

Thorium chloride shows some tendency to combine with alkali or other chlorides to form complexes, which however are not very well defined. Berzelius<sup>1</sup> appears to have obtained a potassium thorium fluoride, to which Cleve<sup>2</sup> attributed the formula  $2\text{ThCl}_4 \cdot \text{KCl} \cdot 18\text{H}_2\text{O}$ , whilst Chydenius<sup>3</sup> obtained the salt  $\text{ThCl}_4 \cdot \text{SNH}_4 \cdot 18\text{H}_2\text{O}$ . Wells and Willis<sup>4</sup> prepared the cesium salts  $3\text{CsCl} \cdot \text{ThCl}_4 \cdot 12\text{H}_2\text{O}$  and  $2\text{CsCl} \cdot \text{ThCl}_4 \cdot 11\text{H}_2\text{O}$ ; but on account of the hygroscopic nature of these compounds there was some uncertainty as to the amount of their water of crystallisation. Chauvenet<sup>5</sup> has prepared a number of double chlorides of thorium and the alkali metals, with and without water of crystallisation. Cleve<sup>6</sup> obtained the platinum compound  $\text{ThCl}_4 \cdot \text{PtCl}_4 \cdot 12\text{H}_2\text{O}$ , and Nilson<sup>7</sup> the compound  $2\text{ThCl}_4 \cdot 3\text{PtCl}_4 \cdot 24\text{H}_2\text{O}$ , the pyridine and quinoline salts  $(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{ThCl}_6$  and  $(\text{C}_8\text{H}_7\text{N})_2 \cdot \text{H}_2\text{ThCl}_6$  respectively, have also been obtained.

**Thorium Bromide**,  $\text{ThBr}_4$  is prepared similarly to the chloride, *i.e.* by the union of its elements, by acting on a heated mixture of thorium and carbon with bromine vapour, and by brominating thorium carbide at high temperature (Moissan and Martinson<sup>8</sup>). It may also be obtained conveniently by the method of Eoumon<sup>10</sup> which is generally applicable to the preparation of anhydrous metallic bromides from their oxides. This method consists in the simultaneous action of sulphur chloride vapour and hydrogen bromide on the metallic oxide heated to a suitable temperature. Thus a white mass of  $\text{ThBr}_4$  is obtained when sulphur chloride vapour at  $135^\circ \text{C}$ . mixed with hydrogen bromide, is distilled on to heated thorium whilst at the temperature is lowered to  $125^\circ \text{C}$   $\text{ThOBr}_2$  results.

Anhydrous thorium bromide forms on sublimation transparent colourless needles of density 5.62. It sublimes *in vacuo* at  $600^\circ$ – $620^\circ \text{C}$ . and boils at about  $725^\circ \text{C}$ . It is hygroscopic and easily soluble in water and alcohol. From a solution of thorium hydroxide in aqueous hydrobromic acid the crystalline hydrate  $\text{ThBr}_4 \cdot 10\text{H}_2\text{O}$  was obtained by Jannasch<sup>11</sup>; other observers have described the hydrates  $\text{ThBr}_4 \cdot 8\text{H}_2\text{O}$ <sup>9</sup> and  $\text{ThBr}_4 \cdot 7\text{H}_2\text{O}$ <sup>12</sup>. According to Chauvenet<sup>13</sup> the double hydrate  $\text{ThBr}_4 \cdot 12\text{H}_2\text{O}$  is obtained in needles by evaporating at  $100^\circ \text{C}$  a solution of thorium hydroxide in alcoholic hydrogen bromide, and this salt when dried in the air passes into  $\text{ThBr}_4 \cdot 10\text{H}_2\text{O}$ , which in a vacuum becomes  $\text{ThBr}_4 \cdot 7\text{H}_2\text{O}$ . The heats of solution of the anhydrous salt and the different hydrates are:  $\text{ThBr}_4$ , 70.190 calories;  $\text{ThBr}_4 \cdot 7\text{H}_2\text{O}$ , 22.550 calories;  $\text{ThBr}_4 \cdot 10\text{H}_2\text{O}$ , 9.810 calories;  $\text{ThBr}_4 \cdot 12\text{H}_2\text{O}$ , 2.300 calories.

<sup>1</sup> Berzelius, *Pogg. Annalen*, 1829, 10, 381.

<sup>2</sup> Cleve, *Bull. Soc. chim.*, 1874 [ii] 21, 116.

<sup>3</sup> Chydenius, *Pogg. Annalen*, 1861, 119, 43.

<sup>4</sup> Wells and Willis, *Amer. J. Sci.*, 1901 [iv] 12, 191.

<sup>5</sup> Chauvenet, *Compt. rend.*, 1909, 148, 1267, 1319.

<sup>6</sup> Cleve, *Bull. Soc. chim.*, 1874, [ii] 21, 116.

<sup>7</sup> Nilson, *Ber.*, 1878, 9, 1056, 1112.

<sup>8</sup> Rosenheim and Schilling, *Ber.*, 1909, 33, 977. See also Rosenheim and Davidsohn, *Zeitsch. anorg. Chem.*, 1904, 35, 121.

<sup>9</sup> Moissan and Martinon, *Compt. rend.*, 1905, 140, 1510.

<sup>10</sup> Eoumon, *Compt. rend.*, 1907, 145, 211.

<sup>11</sup> Jannasch, *Zeitsch. anorg. Chem.*, 1893, 4, 283.

<sup>12</sup> Rosenheim and Schilling, *Ber.*, 1909, 33, 977.

<sup>13</sup> Chauvenet, *Compt. rend.*, 1909, 149, 289.

Thorium bromide forms with ammonia the compound  $\text{ThBr}_4 \cdot 3\text{NH}_3$ ,<sup>1</sup> and with pyridine  $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{ThBr}_6$ .<sup>2</sup>

**Thorium Oxybromide**,  $\text{ThOBr}_2$ , is formed when an aqueous solution of the tetrabromide is evaporated to dryness and the residue is heated to 160° C. (Mossan and Martensen<sup>3</sup>); it is also obtained as a white, amorphous, friable mass by the method of Bourion (see above), and dissolves completely in water with slight hissing. From a solution of thorium hydroxide in alcoholic hydrogen bromide the crystalline hydroxybromides  $\text{Th}(\text{OH})_2\text{Br}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Th}(\text{OH})\text{Br}_3 \cdot 10\text{H}_2\text{O}$  have been obtained.<sup>4</sup>

**Thorium Iodide**,  $\text{ThI}_4$ , was obtained by Nilson<sup>5</sup> by burning the metal in iodine vapour. From a solution of thorium hydroxide in alcoholic hydroiodic acid crystals of the hydroxyiodide  $\text{Th}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$  separate on evaporation *in vacuo* over sulphuric acid, and from the mother-liquor long needles of  $\text{ThI}_4 \cdot 10\text{H}_2\text{O}$  can be obtained.<sup>6</sup>

Thorium chlorate, bromate, iodate, and perchlorate have been prepared by Cleve.<sup>7</sup>

#### THORIUM AND OXYGEN

**Thorium Dioxide** (*Thoria*),  $\text{ThO}_2$ , is obtained by the ignition of the hydroxide, carbonate, sulphate or nitrate, prepared from thorium minerals by the methods already described. It may, however, be obtained in an impure state from thorite or orangite by heating the powdered mineral with carbon in an electric furnace, so as to volatilise the silica.<sup>8</sup> Thoria is a snow-white powder whose physical character varies according to its source; that prepared from the sulphate is dense, that from the nitrate flocculent. It is obtained crystalline by fusion with borax<sup>9</sup> or potassium phosphate<sup>10</sup>; in the former case tetragonal crystals are obtained, in the latter the crystals belong to the regular system. Tetragonal thoria is isomorphous with zirconia, rutile ( $\text{TiO}_2$ ), and cassiterite ( $\text{SnO}_2$ ). The density of crystallised thoria is 10.22.<sup>11</sup> Pure thoria does not glow brightly when heated, nor does it phosphoresce to any extent under the influence of the cathode rays<sup>12</sup>; it has the power of incandescence only when it is mixed with small quantities of other oxides—*e.g.*, for instance, in the incandescent-gas mantle, which contains 99 per cent. of thoria mixed with 1 per cent. of ceria.

Strongly ignited thoria is insoluble in acids, though heating with concentrated sulphuric acid and fusion with potassium hydrogen sulphate convert it into sulphate.

**Metathorium Oxide** is a peculiar, isomeric modification of the oxide, obtained by igniting the oxalate, or the hydroxide precipitated from

<sup>1</sup> Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815, 839.

<sup>2</sup> Rosenheim and Schilling, *Ber.*, 1900, 33, 977.

<sup>3</sup> Mossan and Martensen, *Compt. rend.*, 1905, 140, 2510.

<sup>4</sup> Rosenheim, Samter, and Davidsohn, *Zeitsch. anorg. Chem.*, 1903, 35, 121.

<sup>5</sup> Nilson, *Ber.*, 1882, 14, 2537.

<sup>6</sup> Rosenheim, Samter, and Davidsohn, *Zeitsch. anorg. Chem.*, 1903, 35, 421; Wytouboff and Verneuil, *Ann. Chim. Phys.*, 1905, [vi], 6, 141.

<sup>7</sup> Cleve, *Bull. Soc. chim.*, 1871, [ii], 23, 116.

<sup>8</sup> Troost, *Compt. rend.*, 1893, 116, 1428.

<sup>9</sup> Nordenskiöld and Chydenius, *Pogg. Annalen*, 1880, 110, 612.

<sup>10</sup> Troost and Ouyard, *Compt. rend.*, 1886, 102, 1122.

<sup>11</sup> Nilson, *Ber.*, 1882, 15, 2519.

<sup>12</sup> Crookes, *Proc. Roy. Soc.*, 1881, 32, 206; *Chem. News*, 1881, 43, 237.

dilute solution at low temperature. When hydrochloric or nitric acid is evaporated with this oxide a syrupy residue is obtained which dissolves in water, forming an opalescent liquid. These solutions contain salts of metathorium oxide, which are reprecipitated by the addition of the corresponding acids, in which they are insoluble. These phenomena were first observed by Berlin,<sup>1</sup> Bahr,<sup>2</sup> and Cleve,<sup>3</sup> and it was thought by Bahr that they were due to the oxide of a new metal, whilst Locke<sup>4</sup> considered that the thorina had been reduced to  $\text{Th}_2\text{O}_3$ . The subject has been further investigated by Wyrouboff and Verneuil<sup>5</sup> and by Stevens.<sup>6</sup> According to Wyrouboff and Verneuil<sup>5</sup> the product of the careful ignition of thorium oxalate, nitrate, chloride, or hydroxide is a mixture of two polymetides of thorina, which on account of polymerisation can combine additively with nitric acid to form salts of the empirical composition  $(\text{ThO}_2)_6 \cdot \text{HNO}_3$  and  $(\text{ThO}_2)_5 \cdot 2\text{HNO}_3$ . From analogy with corresponding cerium salts these nitrates are believed to have the molecular composition<sup>6</sup>



Stevens<sup>7</sup> believes that metathorium oxide is not  $\text{Th}_3\text{O}_5$ , but has the same composition as ordinary thorina. When prepared from the oxalate and containing some water it combines with dry hydrogen chloride, forming metathorium oxychloride, which is represented by the formula  $\text{ThO}_2 \cdot x\text{ThCl}_2$ , and dissolves in water, forming a solution which is clear if 9-10 per cent. of chlorine is present, and is opalescent when more basic. It resembles metastannic chloride in properties, and does not give a precipitate with silver nitrate. Metathorium hydroxide is obtained by precipitating the chloride with ammonia; Stevens regards it as metathoric acid and as analogous to metastannic acid.

It would appear from the work of Ruer<sup>8</sup> on colloidal zirconium hydroxide that the reason silver nitrate does not precipitate chloride from metathorium chloride solution is that the latter is colloidal and has the power also of retaining silver chloride in the colloidal form.

**Thorium Hydroxide**,  $\text{Th}(\text{OH})_4$ , is formed as a gelatinous precipitate when a thorium salt solution is mixed with alkali hydroxide. It is insoluble in excess of alkali, but dissolves readily in acids and also in alkali carbonate solutions, forming complex carbonates.

**Thorium Superoxide**,  $\text{Th}_2\text{O}_7$ , is obtained in a hydrated form when ammonia is added to a mixture of thorium acetate or sulphate solution and hydrogen peroxide.<sup>9</sup> This superoxide is rather unstable and easily loses some oxygen, so passing into more stable trioxide,  $\text{ThO}_3$ .<sup>10</sup> By the action of dilute sulphuric acid on the superoxide,  $\text{Th}_2\text{O}_7$ , hydrogen peroxide is formed in solution whilst concentrated sulphuric acid

<sup>1</sup> Berlin, *Pogg. Annalen*, 1852, 85, 555.

<sup>2</sup> Bahr, *Annalen*, 1891, 132, 227.

<sup>3</sup> Cleve, *Bull. Soc. chim.*, 1871, [ii] 21, 116.

<sup>4</sup> Locke, *Zeitsch. anorg. Chem.*, 1891, 7, 345.

<sup>5</sup> Wyrouboff and Verneuil, *Compt. rend.*, 1898, 127, 863, *Ann. Chem. Phys.*, 1905, [viii], 6, 111.

<sup>6</sup> Wyrouboff, however (*Zeitsch. anorg. Chem.*, 1901, 28, 90), regards thorium as bi-valent, and formulates metathorium oxide as  $\text{ThO}^m$ .

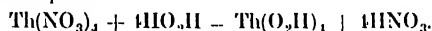
<sup>7</sup> Stevens, *Zeitsch. anorg. Chem.*, 1901, 27, 41.

<sup>8</sup> Ruer, *Zeitsch. anorg. Chem.*, 1905, 43, 85.

<sup>9</sup> Wyrouboff and Verneuil, *Bull. Soc. chim.*, 1897, [iii] 17, 679, 1898, 19, 219, *Compt. rend.*, 1898, 126, 340; 127, 112; *Ann. Chem. Phys.*, 1906, [viii], 6, 441.

<sup>10</sup> Pissarjewski, *Zeitsch. anorg. Chem.*, 1900, 25, 378, 1902, 31, 359, *Calrolau, Atti R. Accad. Sci. Torino*, 1911, 46, 195.

yields ozonised oxygen. The superoxide  $\text{Th}_2\text{O}_7$  is formed by the action of hypochlorite as well as hydrogen peroxide on  $\text{Th}(\text{OH})_4$ , and also by the electrolysis of an alkaline solution of sodium chloride in which thorium hydroxide,  $\text{Th}(\text{OH})_4$ , is suspended. It is therefore regarded by Pissarjewski<sup>1</sup> as a true superoxide, and not merely an addition compound of  $\text{Th}(\text{OH})_4$  and  $\text{H}_2\text{O}_2$ . Its formation from the nitrate is therefore thus represented:



$\text{Th}(\text{O}_2\text{H})_4$  being a salt of hydrogen peroxide, which is subsequently hydrolysed to  $\text{Th}(\text{O}_2\text{H})_2(\text{OH})_2$  and  $\text{Th}(\text{O}_2\text{H})(\text{OH})_3$ , a mixture of which constitutes  $\text{Th}_2\text{O}_7$ .

### THORIUM AND SULPHUR

**Thorium Sulphide**,  $\text{ThS}_2$ , and **Oxysulphide**,  $\text{ThOS}$ . Berzelius<sup>2</sup> obtained a yellow powder and Nilson<sup>3</sup> a black substance by heating thorium in sulphur vapour. Chydenius<sup>4</sup> heated thoria to a high temperature in a stream of hydrogen containing carbon disulphide vapour, and obtained a black product having a density of 8.29. Kruss<sup>5</sup> obtained a brown product, probably the oxysulphide, by the action of hydrogen sulphide on thorium halides; and Hauser<sup>6</sup> prepared the same substance by heating carefully dried thorium sulphate to low redness in a current of hydrogen sulphide. Lastly, Duboin<sup>7</sup> heated a mixture of thorium chloride with excess of sodium or potassium chloride in a porcelain boat contained in a tube through which a current of dry hydrogen sulphide was passed. The product, after washing out the alkali chloride, contained brown lamellae of thorium sulphide,  $\text{ThS}_2$ , having a density of 6.7. After the removal of these lamellae by sifting, the siftings were treated with nitric acid at  $10^\circ \text{C}$ ., which dissolved the remaining  $\text{ThS}_2$  and left the oxysulphide  $\text{ThOS}$  in the form of yellow crystals; these are only very slowly acted on by nitric acid, and have a density of 8.12.

**Thorium Sulphite**,  $\text{Th}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ , was obtained by Cleve<sup>8</sup> as a white precipitate by dissolving the sulphate in sulphurous acid and warming the solution. The solubility of this salt in sodium sulphite solution, with the formation of a complex salt, furnishes a means of roughly separating thorium from cerium, lanthanum, and didymium; for when a neutral solution of the mixed salts is poured into excess of a saturated solution of sodium sulphite nearly the whole of the thorium remains in solution, while the other metals are precipitated.<sup>9</sup> The complex sulphites,  $\text{Th}_2(\text{OH})_2(\text{SO}_3)_3$ ,  $2\text{Na}_2\text{SO}_3 \cdot 22\text{H}_2\text{O}$  and  $\text{Th}(\text{OH})_2\text{SO}_3 \cdot 2\text{K}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$  have been isolated.<sup>10</sup>

**Thorium Sulphate**,  $\text{Th}(\text{SO}_4)_2$ , is obtained in an anhydrous state by dissolving the dioxide in concentrated sulphuric acid and heating the

<sup>1</sup> Pissarjewski, *loc. cit.*

<sup>2</sup> Berzelius, *Pogg. Annalen*, 1829, 16, 385.

<sup>3</sup> Nilson, *ibid.*, 1882, 15, 2537.

<sup>4</sup> Chydenius, *Pogg. Annalen*, 1861, 119, 43.

<sup>5</sup> Kruss, *Zeitsch. anorg. Chem.*, 1894, 6, 49.

<sup>6</sup> Hauser, *Zeitsch. anorg. Chem.*, 1907, 53, 74.

<sup>7</sup> Duboin, *Compt. rend.*, 1908, 146, 815.

<sup>8</sup> Cleve, *Bull. Soc. chim.*, 1874 [11], 21, 116.

<sup>9</sup> Chavastelon, *Compt. rend.*, 1900, 130, 781.

<sup>10</sup> Grossmann, *Zeitsch. anorg. Chem.*, 1905, 44, 229.

solution till the excess of sulphuric acid has been evaporated, or by heating the octahydrate  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ <sup>1</sup> to about 100°. The anhydrous sulphate has a density of 9.225. It dissolves sparingly in concentrated sulphuric acid, forming an acid sulphate, which is also formed when a saturated aqueous solution of the sulphate is precipitated with concentrated sulphuric acid. The thorium hydrogen sulphates  $\text{ThH}_2(\text{SO}_4)_4$ <sup>2</sup> and  $2\text{Th}(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ <sup>3</sup> have been obtained.

Thorium sulphate can be dissolved in ten times its weight of ice-cold water, forming a solution that is metastable with respect to various hydrates. The salt is noteworthy on account of its different hydrates; the following are known:

Emmethydrate, $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ ,	monoclinic prisms isomorphous with $\text{U}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$
Octahydrate, $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,	monoclinic crystals
Hexahydrate, $\text{Th}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	
Tetrahydrate, $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	fine needles, isomorphous with $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
Dihydrate, $\text{Th}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	

These different hydrates have different solubility curves, which have been studied by Roozboom and others<sup>4</sup>. The hydrates with 9 and 4 molecules of water present a contrast in properties, since the solubility of the former increases with rise of temperature whilst that of the latter decreases. Consequently, whilst  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$  crystallises from a solution at low temperature,  $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  will separate from the same solution at high temperature. The solubility curves of the two salts are represented by *AC* and *DE* on the accompanying diagram (Fig. 6). These two curves intersect at *B* (13°C.) at which point both salts are in equilibrium with one and the same saturated solution. If the temperature is lowered from this point the 9-hydrate will separate; if raised, the 4-hydrate. Nevertheless each hydrate can exist in a metastable state, so that the solubility curve of  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$  has been traced up to 55°C. (C), and that of  $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  down to 18°C. (E). Thus, while the true equilibrium between these two salts and their saturated solution occurs at 13°C, there is not necessarily a transformation of one salt into the other through the medium of the solution when this temperature is departed from, though the further the temperature is removed from 13°C, towards 18°C, or 55°C the more likely is it that respective transformation into the 9- or 4-hydrate will take place.

The solubility curve *FG* on the diagram is that of the salt  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ , and the curve *HK* of the salt  $\text{Th}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The salt  $\text{Th}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  separates from the solution at about 100°C.

Under conditions favourable to the production of the emmethydrate it very frequently happens that the octahydrate is obtained. The latter

<sup>1</sup> R. J. Meyer and Gumpertz, *Ber.*, 1905, 38, 817.

<sup>2</sup> Brauner and Pieck, *Zeitsch. anorg. Chem.*, 1904, 38, 322.

<sup>3</sup> Manuelli and Gasparmetti, *Gazz. chim. ital.*, 1903, 32, ii 523.

<sup>4</sup> Roozboom, *Zeitsch. physikal. Chem.*, 1890, 5, 198. See also Demargay, *Compt. rend.*, 1883, 96, 1860; Wyrouboff, *Bull. Soc. franc. Min.*, 1901, 24, 105; Koppel and Holtkamp, *Zeitsch. anorg. Chem.*, 1910, 67, 266; and Koppel, *Zeitsch. anorg. Chem.*, 1910, 67, 293.

<sup>5</sup> According to Dawson and Williams (*Proc. Chem. Soc.*, 1899, 15, 211) the temperature is 47°C.

hydrate, on standing in contact with the solution, becomes converted into the former, but the rate of change is extremely slow.

Technically, the octahydrate is a very important salt. Its solubility in aqueous sulphuric acid at 20°, 30°, and 100° C. is shown graphically in Fig. 7. At 30° C. the octahydrate passes into the tetrahydrate when the concentration of sulphuric acid exceeds 33 per cent. At the same temperature, and with hydrochloric and nitric acids as solvents, the concentrations at which the change of hydration occurs are 19.5 and 31 per cent. respectively, and the solubilities of the hydrate are as follow<sup>1</sup>.

Per cent of Acid	Grams of Th(SO <sub>4</sub> ) <sub>2</sub> per 100 grams of Solution at 30° C.		Per cent of Acid	Grams of Th(SO <sub>4</sub> ) <sub>2</sub> per 100 grams of Solution at 30° C.	
	HCl	HNO <sub>3</sub>		HCl	HNO <sub>3</sub>
0	2.15	2.15	25	1.00	1.22
5	3.50	3.50	30	—	3.70
10	3.10	1.26	35	—	3.00
15	2.35	1.79	40	—	2.35
20	2.15	1.70			

By the prolonged heating of the tetrahydrate with water an insoluble basic sulphate, ThOSO<sub>4</sub>·2H<sub>2</sub>O is produced<sup>2</sup>; the salt ThOSO<sub>4</sub>·H<sub>2</sub>O has also been obtained by heating a concentrated solution of thorium sulphate in a sealed tube at 160–180°C.<sup>3</sup> ThOSO<sub>4</sub>·5H<sub>2</sub>O is also known.<sup>1</sup>

**Complex Thorium Sulphates.** Thorium sulphate unites with the sulphates of the alkali metals to form various complex sulphates. Berzelius<sup>5</sup> appears to have obtained the salt K<sub>4</sub>Th(SO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O by mixing solutions of the constituent sulphates; but Rosenheim, Samter, and Davidsohn<sup>6</sup> state that the anhydrous salt K<sub>4</sub>Th(SO<sub>4</sub>)<sub>3</sub> separates when the solutions are mixed; whilst the following sulphates have been obtained by Barre<sup>7</sup>: Th(SO<sub>4</sub>)<sub>2</sub>·K<sub>2</sub>SO<sub>4</sub>·11H<sub>2</sub>O; Th(SO<sub>4</sub>)<sub>2</sub>·2K<sub>2</sub>SO<sub>4</sub>·21H<sub>2</sub>O; 3Th(SO<sub>4</sub>)<sub>2</sub>·7K<sub>2</sub>SO<sub>4</sub>. From mixed solutions of sodium and thorium sulphates the two salts Na<sub>2</sub>Th(SO<sub>4</sub>)<sub>3</sub>·12H<sub>2</sub>O and Na<sub>4</sub>Th(SO<sub>4</sub>)<sub>3</sub>·11H<sub>2</sub>O have been prepared,<sup>8</sup> and from ammonium and thorium sulphates the salts



The rubidium and caesium salts Rb<sub>2</sub>Th(SO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O and Cs<sub>2</sub>Th(SO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O have also been prepared.<sup>8</sup>

<sup>1</sup> Interpolated from the data of Koppel and Holtkamp, *Zeitsch. anorg. Chem.*, 1910, 67, 260.

<sup>2</sup> Deinauay, *Compt. rend.*, 1883, 96, 1860; Barre, *Compt. rend.*, 1910, 151, 70; Hauser, *Ber.*, 1910, 43, 2776.

<sup>3</sup> Hauser and Wuth, *Zeitsch. anorg. Chem.*, 1908, 60, 242.

<sup>4</sup> Halla, *Zeitsch. anorg. Chem.*, 1912, 79, 260.

<sup>5</sup> Berzelius, *Pogg. Annalen*, 1829, 16, 385.

<sup>6</sup> Rosenheim, Samter, and Davidsohn, *Zeitsch. anorg. Chem.*, 1903, 35, 424.

<sup>7</sup> Barre, *Compt. rend.*, 1910, 150, 1599.

<sup>8</sup> Manuelli and Gasparinetti, *Gazz. chim. ital.*, 1903, 32, ii, 523.

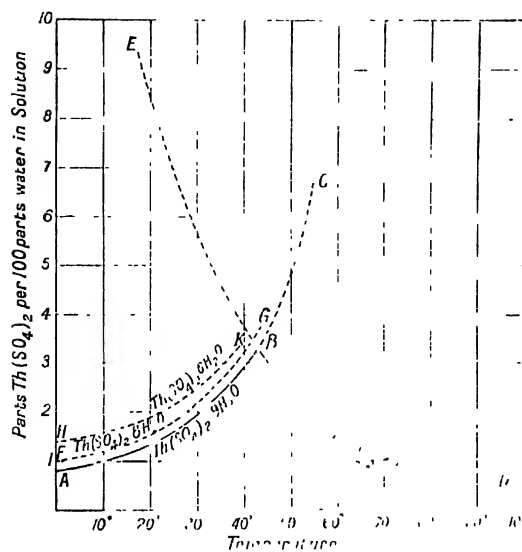


Fig. 6 Solubility curves of the hydrates of thorium sulphate.

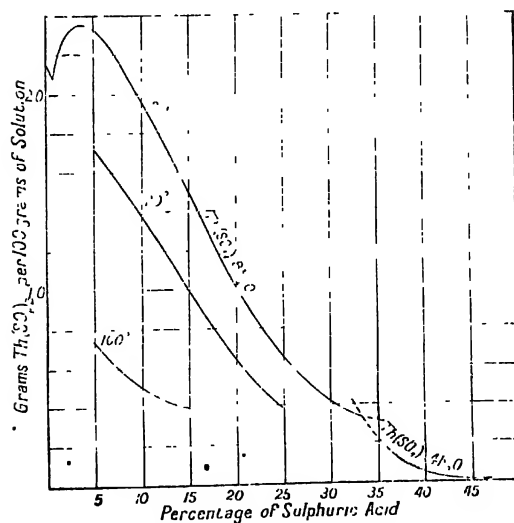


Fig. 7 Solubility of thorium sulphate in sulphuric acid solution.



The double potassium sulphates are slightly soluble in water, but insoluble in a saturated solution of potassium sulphate; the double sodium (and ammonium) salts, on the other hand, are fairly soluble in saturated sodium (and ammonium) sulphate (*e.g.* about 4 parts of  $\text{Na}_2\text{Th}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  per 100 of solution at the ordinary temperature).

#### THORIUM AND SELENIUM

**Thorium Selenite.** The normal salt  $\text{Th}(\text{SeO}_3)_2 \cdot 11\text{H}_2\text{O}$  is a white precipitate<sup>1</sup>; the acid salts  $2\text{ThO}_2 \cdot 7\text{SeO}_2 \cdot 16\text{H}_2\text{O}$  and  $\text{ThO}_2 \cdot 5\text{SeO}_2 \cdot 8\text{H}_2\text{O}$  have also been obtained.<sup>2</sup>

**Thorium Selenate,**  $\text{Th}(\text{SeO}_4)_2 \cdot 9\text{H}_2\text{O}$ , is sparingly soluble in water, and isomorphous with the corresponding sulphate.<sup>3</sup>

#### THORIUM AND THE NITROGEN GROUP

**Thorium Nitride,**  $\text{Th}_3\text{N}_4$ . A nitride of thorium was first obtained as a white powder by Chydenius,<sup>4</sup> who heated a mixture of thorium and ammonium chlorides in a current of hydrogen chloride gas; Moissan and Etard<sup>5</sup> also obtained a nitride by heating the carbide in a stream of ammonia. The nitride may also be prepared by heating a mixture of thoria and magnesium or aluminium in a current of nitrogen,<sup>6</sup> or by strongly heating the metal itself in the same gas.<sup>7</sup> Thus obtained it is a yellowish maroon powder having the composition  $\text{Th}_3\text{N}_4$ ; it is slowly decomposed by cold water, quickly by hot, according to the reaction.



**Thorium Nitrate.** By the crystallisation of a dilute nitric acid solution of thorium hydroxide or carbonate large deliquescent tablets of the salt  $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$  are produced, which are very soluble in water and alcohol. By the crystallisation of a warm aqueous solution the hydrate  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ <sup>8</sup> has been obtained, and from a strongly acid solution the hydrate  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ .<sup>9</sup> A dilute solution of the nitrate is slowly hydrolysed with separation of a basic salt. Thorium nitrate is employed for the manufacture of incandescence-gas mantles. For this purpose it is obtained in granular masses containing about 48 per cent. of thoria, which corresponds nearly to the formula  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ . When strongly ignited the nitrate leaves a residue of pure white oxide. This is dense and harsh when the nitrate is quite pure, but if 1 to 2 per cent. of sulphuric acid is present in the nitrate the salt swells like "Pharaoh's serpents" during ignition, and yields a soft, voluminous ash from six to ten times as bulky as that obtained from the pure nitrate. Most mantle-makers prefer a nitrate that

<sup>1</sup> Cleve, *Bull. Soc. chim.*, 1874, [iii], 21, 116

<sup>2</sup> Nilson, *Ber.*, 1875, 8, 655

<sup>3</sup> Wyrtenhoff, *Zeitsch. Krist. Min.*, 1910, 47, 371

<sup>4</sup> Chydenius, *Pogg. Annalen*, 1861, 119, 13

<sup>5</sup> Moissan and Etard, *Compt. rend.*, 1896, 122, 373. *Ann. Chim. Phys.*, 1897, [viii], 12, 427.

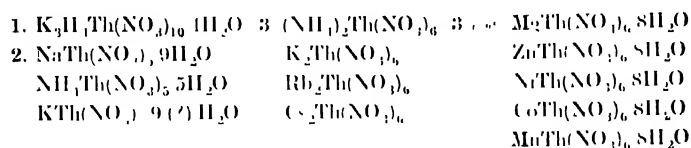
<sup>6</sup> Matignon, *Compt. rend.*, 1900, 131, 891

<sup>7</sup> Matignon and Delépine, *Ann. Chim. Phys.*, 1907, [viii], 10, 130

<sup>8</sup> Fulse, *Zeitsch. angew. Chem.*, 1897, 4, 115

<sup>9</sup> Brauner, *Trans. Chem. Soc.*, 1898, 73, 951.

**Complex Thorium Nitrates.**—The following complex thorium nitrates have been obtained by Meyer and Jacoby<sup>1</sup> by the crystallisation of nitric acid solutions of their constituent salts:



**Thorium Orthophosphate** is practically insoluble in water and only sparingly soluble in dilute acids; its formation therefore serves partially to separate thorium from other metals occurring in monazite sand, whose phosphates are more soluble in dilute sulphuric acid.

According to Cleve<sup>2</sup> the normal phosphate,  $\text{Th}_2(\text{PO}_4)_3 \cdot 4\text{H}_2\text{O}$ , is precipitated when disodium hydrogen phosphate is added to thorium nitrate solution,<sup>3</sup> but Volek<sup>2</sup> has shown that the precipitate contains sodium. Various complex phosphates of thorium and the alkali metals have been described,<sup>4</sup> also the chlorophosphate  $\text{ThCl}_4 \cdot 3\text{ThO}_2 \cdot 2\text{P}_2\text{O}_5$  and the bromophosphate  $\text{ThBr}_4 \cdot 3\text{ThO}_2 \cdot 2\text{P}_2\text{O}_5$ .

**Thorium Arsenates.** Thorium dihydrogen arsenate  $\text{Th}(\text{HAsO}_4)_2 \cdot 6\text{H}_2\text{O}$ , is precipitated in a crystalline form when a 10 per cent. solution of arsenic acid is added to a boiling solution of thorium nitrate containing 2 per cent of thorium. Thorium dihydrogen arsenate,  $\text{Th}(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , is obtained as a crystalline precipitate when a solution of thorium nitrate containing 5 per cent of thorium is treated with a 50 per cent. solution of arsenic acid.<sup>6</sup>

**Thorium Carbide**,  $\text{ThC}_2$ , was first obtained impure by Troost,<sup>7</sup> who heated thorium with carbon in an electric furnace in order to obtain the metal. This compound was prepared in the pure state, however, by Moissan and Etard,<sup>8</sup> who heated in the electric furnace a mixture of 72 grams of thorium and 6 grams of carbon compressed into small cylinders. The current employed was of 900 amperes at 50 volts, and the operation lasted four minutes. The product, examined under the microscope, consisted of yellow transparent crystals mixed with graphite; the density of the carbide at 18° C is 8.96; it burns

<sup>1</sup> B. J. Meyer and Jacoby, *Zoob. Annot. (Linn.)*, 1901, 27, 378.

*Chloro. Bull. Soc. chim.*, 1871, [vol. 21, 116]

<sup>1</sup> Vohlk, *Zeitsch anorg Chem* 1891 6, 141

<sup>1</sup> Trossel and Gayard, *Compt. rend.* 1886, 107, 117; 1887, 105, 30. *Ann. Chim. Phys.*, 1889 [vol. 17, 227].

<sup>5</sup> (Civil Comptrol and 1909, 14), 207

<sup>6</sup> Babinch, *Att. R. k ad. Lucco* 1910, [v] 19, n. 612

<sup>7</sup> Troost, *Compt rend*, 1893, II6, 1227

<sup>8</sup> Moissan and Elaid, *Compt rend.*, 1896, **122**, 573. *Ann Chim Phys.*, 1897, [vol. **12**,

brilliantly when slightly heated in oxygen, and also forms a sulphide, with beautiful incandescence, when heated in sulphur vapour. Concentrated acids have little action on the carbide, dilute acids attack it rapidly, and water reacts with it readily, yielding a mixture of hydrogen with methane, ethane, propane, butane, ethylene, propylene and homologues, and acetylenic hydrocarbons.<sup>1</sup>

**Thorium Carbonate.**—The precipitate obtained by adding sodium carbonate to the solution of a thorium salt is a basic carbonate which dissolves readily in excess of carbonate solution, forming a complex salt. This property serves to distinguish and separate thorium from other rare earths whose carbonates do not so readily dissolve in excess of alkali carbonate. From this solution alcohol precipitates the complex salt  $\text{Na}_6\text{Th}(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$ <sup>2</sup> as a crystalline powder; the following salts have also been obtained<sup>3</sup>:  $\text{K}_6\text{Th}(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Th}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Th}_6(\text{CO}_3)_5$ .

According to Chauvenet<sup>4</sup> thorium oxide absorbs carbon dioxide, forming orthocarbonates. Under ordinary pressure the compound  $2\text{Th}(\text{OH})_4 \cdot \text{CO}_2$  is produced, but under 30–40 atmospheres the orthocarbonate  $\text{ThCO}_3 \cdot 2\text{H}_2\text{O}$ . Under this latter pressure the anhydrous oxide yields  $\text{ThCO}_3 \cdot 6\text{ThO}_2$ . The addition of sodium carbonate to a thorium salt solution forms  $\text{ThCO}_3 \cdot 8\text{H}_2\text{O}$ , which loses  $6\text{H}_2\text{O}$  in a vacuum, and on heating to  $120^\circ \text{C}$ . forms the basic salt  $2\text{ThCO}_3 \cdot 2\text{ThO}_2 \cdot 3\text{H}_2\text{O}$ .

The following thorium salts of organic acids are known:

**Thorium Formate**,  $\text{Th}(\text{CHO}_2)_4 \cdot 3\text{H}_2\text{O}$ , crystallising in colourless plates; and the basic formate  $\text{Th}(\text{OH})_2(\text{CHO}_2)_2$ , which separates as a crystalline precipitate when a dilute thorium salt solution is boiled with sodium formate.<sup>5</sup>

**Thorium Acetate**,  $\text{Th}(\text{C}_2\text{H}_3\text{O}_2)_4$ , separates in fine needles from a solution of thorium hydroxide in acetic acid or of the sulphate in ammonium acetate solution.<sup>6</sup> The basic salt  $\text{Th}(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$  exists.<sup>5</sup>

**Thorium Oxalate** is precipitated when oxalic acid is added to a thorium salt solution. When obtained from hot solutions containing about 10 per cent. of hydrochloric acid the precipitate is dense and crystalline; from cold and nearly neutral solutions the oxalate separates as a rather bulky, amorphous precipitate which readily passes into colloidal solution when washed with water. The composition of the air-dried salt is expressed by the formula  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ <sup>7</sup>; when heated to  $100^\circ \text{C}$ . or dried over sulphuric acid the dihydrate  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  is formed, and at  $160^\circ \text{C}$ . the hydrate  $\text{Th}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$  is obtained.<sup>8</sup>

Thorium oxalate is practically insoluble in water and aqueous oxalic acid, and is much less soluble in dilute mineral acids than the oxalates of the trivalent rare earth elements.<sup>9</sup> The solubility in aqueous sulphuric acid at  $25^\circ \text{C}$ . is as follows<sup>10</sup>:

<sup>1</sup> Lebeau and Damiens, *Compt. rend.*, 1913, 156, 1987.

<sup>2</sup> Cleve, *Bull. Soc. chim.*, 1874, [n], 21, 118.

<sup>3</sup> Rosenheim, Samter, and Davidsohn, *Zeitsch. anorg. Chem.*, 1903, 35, 424.

<sup>4</sup> Chauvenet, *Compt. rend.*, 1911, 153, 66.

<sup>5</sup> Haber, *Monatsh.*, 1897, 18, 687.

<sup>6</sup> Urbain, *Bull. Soc. chim.*, 1896, [m], 15, 338, 347.

<sup>7</sup> Brauner, *Trans. Chem. Soc.*, 1898, 73, 984.

<sup>8</sup> Hauser and Wuth, *Zeitsch. anorg. Chem.*, 1912, 78, 75.

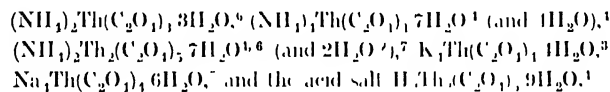
<sup>9</sup> Brauner, *Trans. Chem. Soc.*, 1898, 73, 972. See also this series, vol. iv, p. 273.

<sup>10</sup> Hauser and Wuth, *Zeitsch. anal. Chem.*, 1908, 47, 389, and *loc. cit.*, Wuth, *Zeitsch. anorg. Chem.*, 1912, 76, 174.

Normality of $\text{H}_2\text{SO}_4$ . . . . .	1	3.2	4.56	6.4	6.94
Grams of $\text{Th}(\text{C}_2\text{O}_4)_2$ per 100 grams of solution . . . . .	0.019	0.070	0.154	0.233	0.276

With higher concentrations of sulphuric acid the oxalate is changed into sulphate. Hydrochloric acid in concentrations greater than about 20 per cent. converts the oxalate into an oxalochloride,  $\text{Th}_4(\text{C}_2\text{O}_4)_6\text{Cl}_4 \cdot 20\text{H}_2\text{O}$ .<sup>1</sup> The solubility of thorium oxalate in dilute mineral acids is reduced to a negligible amount by the addition of a moderate excess of oxalic acid.

A characteristic property of thorium oxalate is its power to combine with alkali oxalates to form complex salts, and this furnishes a method of distinguishing and separating thorium from other metals of the rare earths.<sup>2</sup> The following complex salts have been described:



According to Hauser and Wirth, the salts  $(\text{NH}_4)_4\text{Th}(\text{C}_2\text{O}_4)_4 \cdot 7\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Th}_2(\text{C}_2\text{O}_4)_7 \cdot 7\text{H}_2\text{O}$  are labile phases in the system thorium oxalate - ammonium oxalate - water at 25° C., the stable phases, in addition to the single oxalates, being the other salts mentioned above. The heptahydrate, which crystallises from a concentrated solution of thorium oxalate in a large excess of ammonium oxalate, passes into the tetrahydrate in dry air, and the latter salt may be dehydrated over phosphoric oxide. At the ordinary temperature 100 parts of water dissolve 90.3 parts of the tetrahydrate, but an extra 9.3 parts of ammonium oxalate must be present in solution to prevent decomposition of the double salt by water. When a solution of this salt in water is diluted with much water it becomes turbid, and a colloidal precipitate, which slowly becomes crystalline, is produced. The precipitate is the salt  $(\text{NH}_4)_2\text{Th}_2(\text{C}_2\text{O}_4)_7 \cdot 7\text{H}_2\text{O}$ . Further work on these double salts, from the physicochemical standpoint, is desirable, since the results of Hauser and Wirth are not in accordance with those of James, Whittemore, and Holden.

**Thorium Tartrate.** If a solution of tartaric acid is added to a thorium salt solution a precipitate is formed which dissolves in excess of the acid. On diluting this solution a tartrate is reprecipitated which, according to Cleve,<sup>3</sup> has the composition  $\text{Th}_2(\text{OH})_4(\text{C}_4\text{H}_4\text{O}_6)_4 \cdot 5\text{H}_2\text{O}$ . By mixing in solution equivalent quantities of thorium nitrate and tartaric acid a tartrate of the composition  $\text{Th}_2\text{O}_2(\text{C}_4\text{H}_4\text{O}_6)_4 \cdot 20\text{H}_2\text{O}$  is precipitated; and this may be represented as the thorium salt of thiorotartronic acid, thus:  $[\text{ThO}(\text{C}_4\text{H}_4\text{O}_6)_2]_2\text{Th} \cdot 20\text{H}_2\text{O}$ .<sup>5</sup> Various thiorotartrates have been prepared. Thus by saturating a boiling solution of potassium hydrogen tartrate with thorium hydroxide Cleve<sup>3</sup> obtained  $\text{K}_4\text{Th}(\text{C}_4\text{H}_4\text{O}_6)_3$ , and Rosenheim, Samter, and Davidsohn<sup>6</sup>

<sup>1</sup> Hauser and Wirth, *loc. cit.*

<sup>2</sup> Bunsen, *Poly. Union*, 1875, 155, 375; Brauner, *Trans. Chem. Soc.*, 1898, 73, 951.

<sup>3</sup> Cleve, *Bull. Soc. chim.*, 1874 [3], 21, 116.

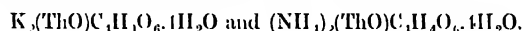
<sup>4</sup> Brauner, *loc. cit.*

<sup>5</sup> Rosenheim, Samter, and Davidsohn, *Z. phys. anorg. Chem.*, 1903, 35, 421.

<sup>6</sup> Hauser and Wirth, *ibid.*, 1912, 78, 75.

<sup>7</sup> James, Whittemore, and Holden, *J. Amer. Chem. Soc.*, 1914, 36, 1853.

have prepared  $\text{ThO}(\text{C}_4\text{H}_4\text{O}_6\text{K})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{ThO}(\text{C}_4\text{H}_4\text{O}_6\text{Na})_2 \cdot 8\text{H}_2\text{O}$ , and  $\text{ThO}(\text{C}_4\text{H}_4\text{O}_6\text{NH}_4)_2 \cdot 3\text{H}_2\text{O}$ , as well as the more basic salts



The constitution of these salts is probably analogous to that of tartar emetic, so that the hydroxylic hydrogen atoms of tartaric acid are replaced by ThO.

**Thorium Acetylacetonate**,  $\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4$ .—In common with other rare earth metals, thorium forms a solid compound with acetylacetonate. It is obtained by the action of acetylacetonate on thorium hydroxide, of sodium acetylacetonate on thorium salts,<sup>1</sup> or in nearly quantitative yield by adding a solution of a thorium salt to a faintly alkaline solution of acetylacetonate, and precipitating with the smallest quantity of ammonia.<sup>2</sup> The product can be crystallised from alcohol, melts at 171° C., and may be sublimed under reduced pressure without appreciable decomposition; its molecular weight<sup>3</sup> in carbon tetrachloride solution confirms the formula  $\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4$ . With ammonia it forms the addition compound  $[\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4]_2 \cdot \text{NH}_3$ . The stereochemical constitution of thorium and other metallic acetylacetonates presents an interesting problem.<sup>4</sup>

#### THORIUM AND SILICON

**Thorium Silicide**,  $\text{ThSi}_2$ , is prepared by heating in a magnesia crucible, to 1200° C., an intimate mixture of 15 grams potassium thorfluoride, 60 grams potassium silicofluoride, and 50 grams aluminum, the product being freed from aluminum and silicon by treatment with potassium carbonate solution. It may also be prepared by heating a mixture of thorina and silicon in an electric furnace, or by heating a mixture of aluminum, silicon, and thorium to 1000° C.<sup>5</sup> It forms quadratic plates, resembling graphite, and has a density of 7.96 at 16° C. It is soluble in aqueous mineral acids, but not in aqueous alkalis.

**Thorium Silicate**. The minerals thorite and orangite contain thorina combined with silica, and artificial silicates corresponding to the formulae  $\text{ThSiO}_4$  and  $\text{ThSi}_2\text{O}_6$ <sup>6</sup> have been prepared by fusing together thorina and silica.

#### THORIUM AND BORON

**Thorium Borides**. When a mixture of thorina with boron is heated in a carbon boat in an electric furnace a bronze-yellow to red product is obtained from which two borides of thorium,  $\text{ThB}_4$  and  $\text{ThB}_6$ , can be isolated.<sup>7</sup>

**Thorium Tetraboride**,  $\text{ThB}_4$ , is a yellow, metallic-looking powder consisting of fragments of prismatic crystals, and having a density of

<sup>1</sup> Urban, *Bull. Soc. chim.*, 1896, [iii], 15, 338, 347. *Ann. Chim. Phys.*, 1900, [vii], 19, 184.

<sup>2</sup> Biltz, *Annalen*, 1904, 331, 334. *Zeitsch. anorg. Chem.*, 1904, 40, 218.

<sup>3</sup> Hongschmid, *Compt. rend.*, 1906, 142, 157.

<sup>4</sup> See Morgan and Moss, *Trans. Chem. Soc.*, 1911, 105, 189.

<sup>5</sup> Hongschmid, *ibid.*, see also Wedekind and Fierz, *Chem. Zeit.*, 1905, 29, 1031.

<sup>6</sup> Troost and Ouvrard, *Compt. rend.*, 1887, 105, 255. *Ann. Chim. Phys.*, 1889, [vi], 17, 227.

<sup>7</sup> Buet du Jassonneux, *Compt. rend.*, 1905, 141, 191. *Ann. Chim. Phys.*, 1909, [viii], 17, 145.

7.5 at 15° C. It is dissolved by cold hydrochloric and nitric acids and by hot sulphuric acid.

**Thorium Hexaboride**,  $\text{ThB}_6$ , is an amorphous, reddish violet, metallic-looking substance having a density of 6.1 at 15° C. It is not dissolved by concentrated hydrochloric and sulphuric acids, but dissolves readily in hot nitric acid.

#### DETECTION AND ESTIMATION OF THORIUM<sup>1</sup>

**Detection of Thorium.** The following qualitative reactions are characteristic of thorium:

*Alkali hydroxide, ammonia, and ammonium sulphide* solutions precipitate from thorium salt solutions the hydroxide  $\text{Th}(\text{OH})_4$ , insoluble in excess of the precipitant. *Alkali carbonates* precipitate basic thorium carbonate, soluble in excess; *potassium sulphate* precipitates  $\text{K}_2\text{Th}(\text{SO}_4)_4$ , soluble with difficulty in water, and distinguished from the corresponding yttrium salt by insolubility in excess of the precipitant. *Oxalic acid* precipitates the oxalate, insoluble in excess of the precipitant (distinction from zirconium); *ammonium oxalate* also precipitates the oxalate, but redissolves it when added in excess, forming a solution not precipitated by dilution (distinction from cerium and yttrium); *hydrochloric acid*, however, reprecipitates the oxalate from this solution, since the latter is insoluble in oxalic acid (distinction from zirconium). *Sodium thiosulphate* on boiling precipitates all the thorium from a solution (preferably of the chloride) as basic thorium thiosulphate (distinction from cerium and yttrium metals). *Potassium iodate* precipitates thorium as the iodate; precipitation is complete even in a solution containing 10 per cent. by volume of concentrated nitric acid provided a moderate excess of precipitant is added (distinction from rare earth metals except zirconium and quadrivalent cerium).<sup>2</sup> *Sodium hypophosphate* precipitates the corresponding thorium salt, insoluble in dilute mineral acids.<sup>3</sup> *Sodium pyrophosphate* precipitates the thorium salt, practically insoluble in dilute (0.5 N) mineral acids (distinction from rare earth metals except zirconium and quadrivalent cerium).<sup>4</sup>

**Estimation of Thorium.** Thorium is always estimated gravimetrically as oxide formed by the ignition of the hydroxide, superoxide, or oxalate. The oxide should be perfectly white; traces of "didymium" oxide impart to it a pink or brownish tint. It is very hygroscopic.

There is little difficulty in separating thorium quantitatively from all other metals except those of the rare earths. For the separation from these metals numerous methods have been proposed. They are enumerated in Volume IV (Chapter XI) of this series, where full references to the literature are given.

The determination of thorium in monazite sand is an important one. Owing to the presence of large amounts of other rare earth metals and phosphoric acid, the estimation is rather difficult and tedious. The only methods which do not necessitate removal of the phosphoric acid are precipitation as iodate, hypophosphate or pyrophosphate and all the

<sup>1</sup> See Meyer and Hauser, *Die chemische Analyse der seltenen Erden* (Stuttgart, 1912).

<sup>2</sup> R. J. Meyer and Später, *Chem. Zeit.*, 1910, 34, 306; R. J. Meyer, *Zeitsch. anorg. Chem.*, 1911, 71, 65.

<sup>3</sup> Koss, *Chem. Zeit.*, 1912, 36, 686; Rosenheim, *ibid.*, 1912, 36, 821. Wirth, *ibid.*, 1913, 37, 773.

<sup>4</sup> Carney and Campbell, *J. Amer. Chem. Soc.*, 1914, 36, 1134.

methods available necessitate a second precipitation of the thorium to remove small amounts of other rare earths carried down with the first precipitate. The sand is weighed, "broken" by being heated with excess of concentrated sulphuric acid to 200° C. for several hours, cooled, and the product poured into a large volume of cold water. From the cold filtered solution the rare earth metals are precipitated by an excess of oxalic acid. The washed oxalate precipitate is decomposed by ignition, by boiling it with sodium hydroxide, or by heating it with a mixture of concentrated and fuming nitric acid. The oxide or hydroxide may then be dissolved in hydrochloric acid, the thorium separated by double precipitation as the basic thiosulphate, the precipitate dissolved in hydrochloric acid, the solution filtered from sulphur, precipitated as oxalate and ignited to oxide; or the nitrate solution may be neutralized with ammonia, precipitated with hydrogen peroxide as hydrated thorium peroxide, and the precipitate changed into thorina by ignition.<sup>1</sup>

In acetic acid solution, thorium may be determined by titration with ammonium molybdate solution, using diphenylcarbazide as an external indicator. Trivalent rare earth elements do not interfere.<sup>2</sup>

#### THE RADIOACTIVITY OF THORIUM

**Discovery of the Radioactivity of Thorium.**—The radioactivity of thorium was discovered in 1898 by Madame Curie<sup>3</sup> and by Schmidt,<sup>4</sup> independently. Becquerel<sup>5</sup> had observed the radioactivity of uranium in 1896; and when a careful examination of other elements for a similar phenomenon was made, the only one which yielded results was thorium. Thorium was found to resemble uranium in its power of ionising a gas and discharging an electroscope, but was several times less active, photographically, than the latter element. The reason for this difference between the radioactivity of the two elements is that whilst both emit similar  $\alpha$ -radiations, the  $\beta$ -radiation of thorium, which possesses photographic activity, is much weaker than that of uranium. It is noteworthy that the radioactivity of thorium was observed previous to the discovery of radium itself.

**Thorium-X.** The discovery of thorium-X followed that of uranium-X. In 1900 Crookes<sup>6</sup> found that when a solution of a uranium salt is precipitated with ammonium carbonate, which is then added in excess, nearly but not quite all the precipitate is redissolved; and that in the

<sup>1</sup> The literature relating to the analysis of monazite sand is as follows

Boudouard, *Compt. rend.*, 1895, **121**, 273; *Bull. Soc. chim.*, 1898, [iii], **19**, 10; Frezenius and Hintz, *Zeitsch. anal. Chem.*, 1896, **35**, 525; Glaser, *J. Amer. Chem. Soc.*, 1896, **18**, 782; *Chem. Zeit.*, 1896, **20**, 612; *Zeitsch. anal. Chem.*, 1897, **36**, 213; 1898, **37**, 25; Hintz and Weber, *ibid.*, 1897, **36**, 27, 676; Hintz, *ibid.*, 1898, **37**, 94, 504; Drossbach, *Zeitsch. angew. Chem.*, 1901, **14**, 655; Benz, *ibid.*, 1902, **15**, 297; Hauser and Wirth, *ibid.*, 1909, **22**, 484; Metzger, *J. Amer. Chem. Soc.*, 1902, **24**, 901; Neish, *ibid.*, 1904, **26**, 780; Carney and Campbell, *ibid.*, 1914, **36**, 1134; Borelli, *Gazzetta*, 1909, **39**, i, 425; R. J. Meyer and Später, *Chem. Zeit.*, 1910, **34**, 306; Johnstone, *J. Soc. Chem. Ind.*, 1914, **33**, 55; R. C. Wells, *ibid.*, 1910, **29**, 1301; White, *Thorium and its Compounds* (The Institute of Chemistry, 1912).

<sup>2</sup> Metzger and Zons, *J. Ind. Eng. Chem.*, 1912, **4**, 493.

<sup>3</sup> Madame Curie, *Compt. rend.*, 1898, **126**, 1,01.

<sup>4</sup> Schmidt, *Ann. Phys.*, 1898, **65**, 141.

<sup>5</sup> Becquerel, *Compt. rend.*, 1896, **122**, 420.

<sup>6</sup> Crookes, *Proc. Roy. Soc.*, 1900, **66**, 409.

small amount of residue there is concentrated for the time being the whole of the photographic activity of the original salt.

Rutherford and Soddy<sup>1</sup> made analogous observations on thorium in 1902. They found that when a solution of pure thorium nitrate is precipitated by ammonia, or when thorium oxide is washed repeatedly with water, the aqueous filtrate or washings yield on evaporation a residue chemically free from, but several thousand times as radioactive as, the original thorium, whilst the radioactivity of the latter has appreciably diminished during the process. This powerfully radioactive product was named thorium-X. If sodium hydroxide or ammonium carbonate or oxalate is employed instead of ammonia to precipitate the thorium, no separation between thorium and thorium-X is effected, the precipitated thorium compound retains its original activity, and the filtrate is not radioactive. Thus there is a distinct chemical difference between thorium and thorium-X, since ammonia precipitates the former, but not the latter, whilst sodium hydroxide precipitates both. The actual amount of thorium-X fractionally separated from thorium is, however, so minute as to be detected only by its radioactivity.

**Decay and Recovery of Radioactivity.** A remarkable relationship found to exist between uranium and uranium-X led to the discovery of a similar relationship between thorium and thorium-X. Becquerel<sup>2</sup> had discovered that a non-active uranium solution from which uranium-X had been separated fractionally, regained its original radioactivity within a year, whilst the radioactive uranium-X lost its activity during the same time. Rutherford and Soddy made similar observations with thorium. They found that thorium from which thorium-X had been separated regained its full activity within a month, and that the thorium-X lost nearly all its activity during the same time.

The accompanying diagram (Fig. 8) shows the rate of decay of activity of thorium-X and the rate of recovery of activity by (almost) inactive thorium. It will be observed that the curves are reciprocal, and that the sum of the two activities remains constant during the whole time. Thus in the figure the sum amounts to about one hundred units. This explains why the activity of natural thorium is constant; it is the result of two reciprocal processes, which together maintain what is called *radioactive equilibrium*.

It may be remarked that the curves are *exponential* or *logarithmic*; they represent a process analogous to that of a continuous monomolecular chemical change, the change at any instant being a constant fraction of what remains to be changed.

When thorium-X was first investigated, and was thought to be produced directly from thorium, it was found that the thorium did not become perfectly inactive by the removal of thorium-X. A "non-separable activity" remained, consisting of  $\alpha$ -rays only, which were 25 per cent. of the total  $\alpha$ -radiation. The cause of this non-separable activity became evident later, when disintegration products intervening between thorium and thorium-X were brought to light.

The observation that thorium-X is spontaneously regenerated in

<sup>1</sup> Rutherford and Soddy, *Trans. Chem. Soc.*, 1902, 81, 321, 837.

<sup>2</sup> Becquerel, *Compt. rend.*, 1900, 131, 127, 1901, 133, 977.



a thorium solution from which it has been separated led to the origination of the disintegration theory of radioactivity.

**The Thorium Emanation.**—A short time previous to the work on thorium-X it was observed by Owens<sup>1</sup> that the radioactivity of thorium varies in a manner traceable to the production of a radioactive gas which can be carried away by currents of air. Such an observation was bound to modify profoundly the ordinary view of the nature of the chemical atom. So long as radioactivity appeared to be a constant property of an atom, and its nature remained imperfectly understood,

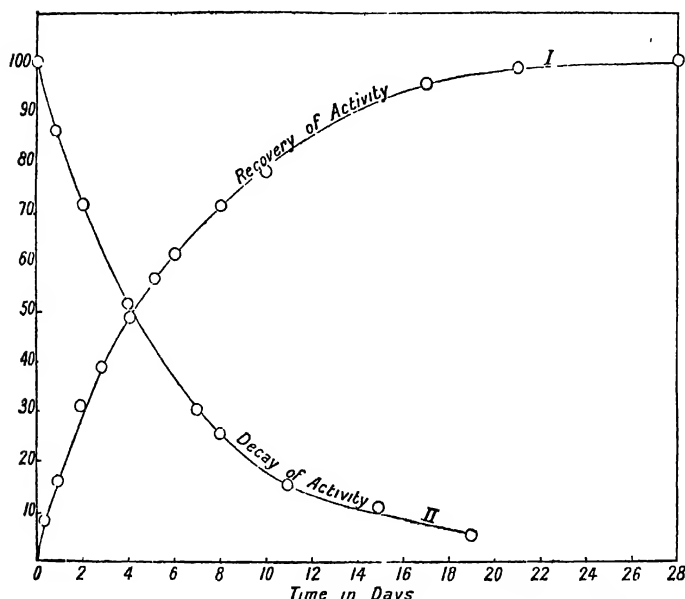


FIG. 8.—Decay of activity of thorium-X and recovery of activity by thorium (Rutherford and Soddy, *Phil. Mag.*, 1902, [vi], 4, 378.)

it was possible to cling to the belief in the unalterability of the atom. But when it was found that atoms of thorium spontaneously produce atoms of radioactive matter, which are gaseous, such belief became untenable.

Rutherford<sup>2</sup> first showed, by an electrical method, that in addition to emitting  $\alpha$ - and  $\beta$ -rays thorium compounds impart to the surrounding air the property of temporary radioactivity, which is retained by the air for a short time after the removal of the thorium compound from its vicinity. This temporary radioactivity rapidly diminishes, however. At the end of a minute it is reduced to a half, and at the end of ten minutes to one-thousandth its original intensity. Paper or thin metal-

<sup>1</sup> Owens, *Phil. Mag.*, 1899, [v], 48, 360.

<sup>2</sup> Rutherford, *Phil. Mag.*, 1900, [v], 49, 1.

leaf does not prevent a thorium compound from imparting this property to the air, and cotton-wool and dilute and concentrated sulphuric acid do not interfere with the action, but a thin sheet of mica or other material which will stop the passage of a gas, entirely prevents the air in the neighbourhood of a thorium compound becoming radioactive. These facts clearly showed that thorium emits a radioactive gas. Rutherford called this gas the **thorium emanation**. It diffuses like any other gas; it is chemically inert and is therefore allied to the argon family of gases; it may be condensed to a liquid in a tube cooled with liquid air, since radioactivity is arrested under this treatment and is apparent again when the cooling agent is removed. The condensation begins at  $-120^{\circ}\text{C}$  and is complete<sup>1</sup> at  $-155^{\circ}\text{C}$ .

The coefficient of diffusion of the thorium emanation is 0.1, so that the gas has a high molecular weight, which by the method of diffusion has been shown to lie between 200 and 210.<sup>2</sup> The emanation is derived not directly from thorium, but from thorium-X, because thorium from which thorium-X has been removed has also lost thereby its emanating power, which it regains as it regenerates thorium-X with its accompanying radioactivity.

The thorium emanation has an unvarying rate of decay represented by the equation

$$\frac{I_t}{I_0} = e^{-\lambda t}$$

in which  $I_0$  is the initial activity,  $I_t$  the activity after  $t$  seconds,  $e$  the base of natural logarithms, and  $\lambda$  the *radioactive constant*, the determining factor of the change. This constant represents the fraction of the whole which undergoes change per second, whilst its reciprocal  $\frac{1}{\lambda}$  represents the average life of the active matter expressed in seconds. The value of  $\lambda$  for the thorium emanation was determined to be  $\frac{1}{87}$ , the period of average life being thus 87 seconds. A recent value is 78.69 seconds, which corresponds to a half-decay period of 51.53 seconds.<sup>3</sup>

The recovery of emanating power by thorium from which thorium-X has been removed is represented by the equation

$$\frac{I_t}{I_0} = 1 - e^{-\lambda t}$$

and the curves showing the decay of the emanation and the above recovery are of the same character as those shown in Fig. 8.

**The Active Deposit.** It was observed by M. and Mme. Curie,<sup>4</sup> in 1899, that radium has the power of "exciting" or "inducing" temporary radioactivity on the surface of neighbouring bodies; and a similar observation with regard to thorium was made independently by Rutherford.<sup>5</sup> Thus the whole interior surface of a closed vessel containing a radium or thorium preparation becomes radioactive; but if an electric field is created inside the vessel all the radioactivity may be concentrated upon the negative electrode. That the excited

<sup>1</sup> Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], 5, 501.

<sup>2</sup> Miss Lashie, *Compt. rend.*, 1911, 153, 328.

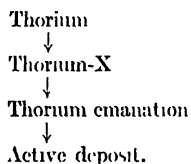
<sup>3</sup> Perkins, *Phil. Mag.*, 1914, [vi], 27, 720.

<sup>4</sup> M. and Mme. Curie, *Compt. rend.*, 1899, 129, 711.

<sup>5</sup> Rutherford, *Phil. Mag.*, 1900, [v], 49, 1-16d.

activity is connected with the emanation is proved by the fact that a sheet of mica, which screens off the emanation, also prevents the production of the excited activity. Indeed, it was found that the amount of the emanation conveyed in a current of the air and the degree of excited activity produced are quantitatively related. It was further observed by Rutherford that the activity excited on a platinum wire exposed to the thorium emanation can be dissolved from the wire, and so be obtained in solution, by means of dilute or concentrated hydrochloric or sulphuric acid. Thence it was concluded that the excited activity is due to a deposit of radioactive matter possessing specific chemical properties, and derived from the emanation. This deposit is therefore spoken of as the "active deposit"; and the thorium emanation is the parent of the active deposit, just as thorium-X is the parent of the emanation. The excited activity decays, and recovers its strength through the agency of the emanation, according to the same principles as those already referred to; and the same equations represent the curves of decay and recovery.

In 1904 the following was the state of knowledge regarding the radioactivity of thorium:



**Radiothorium and Mesothorium.**—In fractionating a mixture of bromides from thorianite, Hahn,<sup>1</sup> in 1905, discovered that not only the radioactivity of the least soluble fractions increased on account of the radium within them, but also that of the most soluble fractions; and subsequently this observer isolated a few milligrams of an intensely active substance which produced seven hundred thousand times as much thorium emanation per unit-time as thorium itself. Similar observations were made by Ramsay,<sup>2</sup> who worked up 250 kilograms of the mineral, and by fractionating 18 grams of alkaline-earth carbonates thence obtained, observed that activity became concentrated both in the more and the less soluble fractions, leaving the middle fraction less active.<sup>3</sup> The new product was found to be at least one hundred thousand times as active as thorium, and was called, on account of its intensity, **radiothorium**. The following disintegration series was proposed by Ramsay:



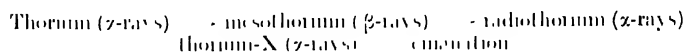
and thus a product intermediate between thorium and thorium-X was recognised, with chemical properties closely allied to those of thorium. It remained uncertain, however, whether thorium was really the parent of radiothorium, or whether another product intervened between these two.

<sup>1</sup> Hahn, *Zeitsch. physikal. Chem.*, 1905, 51, 717.

<sup>2</sup> Ramsay, *J. Chim. phys.*, 1905, iii, 817.

<sup>3</sup> See also Hahn, *Ber.*, 1905, 38, 3371; 1907, 40, 1462, 3304; *Jahrb. Radioakt. Elek.*, 1905, [ii], 233; Elster and Geitel, *Physikal. Zeitsch.*, 1906, 7, 143.

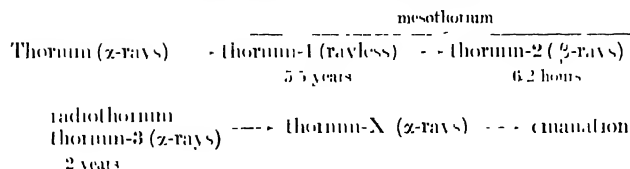
In 1906 Blane<sup>1</sup> succeeded in separating from ordinary thorium compounds, radiothorium, comparable in activity with the product obtained from thorium; and in the same year Hahn<sup>2</sup> brought forward evidence of the existence of an inactive disintegration product intermediate between thorium and radiothorium. He found that the activity of thorium salts, e.g. the nitrate, prepared from thoriumite, diminishes for three years, remains constant for some time, and then again increases, and explained the occurrence by supposing that in the preparation of thorium nitrate from thoriumite an existing intermediate product, which he called **mesothorium**, is left behind, so that a  $\zeta$ ,  $\eta$  exists between thorium and radiothorium and that the equal rates of formation and decay of inactive mesothorium are greater than those times of radiothorium. Hence the more rapid decay of existing radiothorium in the initial absence of mesothorium leads to a diminution of activity, followed at length by an increase when the accumulation of fresh and more slowly formed mesothorium gives rise to a regeneration of radiothorium. Hahn<sup>2</sup> confirmed this conclusion by eliminating thorium, and thus obtaining an inactive product (mesothorium), which after a lapse of time developed the activity of radiothorium. Subsequently<sup>3</sup> the same observer stated the changes taking place between thorium and the emanation to be as follows:



It will be remembered that 25 per cent. of the total z-radiation of natural thorium remained originally after the removal of thorium-X. This considerable activity was subsequently thought to belong to radiothorium thorium itself being rayless. Attention must therefore be drawn to the fact that the thorium atom is now shown to emit z-rays in its disintegration.

In 1908 a further step was taken by Hahn<sup>4</sup> in the recognition of a short-lived product between mesothorium and radiothorium. By adding ammonia to a mesothorium solution freed from radiothorium and containing a little zirconium salt, Hahn obtained a precipitate possessing a  $\beta$ -radiation which decayed to zero in a few hours, and a filtrate, which was at first inactive, but developed  $\beta$ -rays with the same period as that at which the  $\beta$ -rays of the precipitated fraction decayed. So it was concluded that the mesothorium had been separated by the ammonia into two constituents which were at first called *thorium-1* and *thorium-2*, and the former of which was rayless while the latter product emitted  $\beta$ -rays. The period of half-change of thorium-2 was estimated to be 6.2 hours, the half-period of radiothorium is 737 days or almost exactly two years<sup>5</sup>, whilst that of thorium-1 is calculated to be 5.5 years<sup>6</sup>. The following scheme now represents the series of changes between thorium and the emanation.

<sup>1</sup> Blane, *Physikal. Zeitsch.*, 1906, 7, 620; *Utt. R. Acad. Lincei*, 1907, [v], 16, 1, 291.  
<sup>2</sup> Hahn, *Ber.*, 1907, 40, 1462.  
<sup>3</sup> Hahn, *Ber.*, 1907, 40, 1304.  
<sup>4</sup> Hahn, *Physikal. Zeitsch.*, 1908, 9, 213 and 216.  
<sup>5</sup> Blane, *Utt. R. Acad. Lincei*, 1907, [v], 16, 1, 291.  
<sup>6</sup> McCoy and Ross, *J. Amer. Chem. Soc.*, 1907, 29, 1709; Hahn, *Physikal. Zeitsch.*, 1908, 9, 392.



The terms thorium-1, thorium-2, and thorium-3 have not been retained, those in present use being respectively **mesothorium-1**, **mesothorium-2**, and **radiothorium**.

The total  $\alpha$ -activity of thorium in equilibrium with all its products is made up of 11 per cent. due to thorium itself, 20 per cent. due to radiothorium, and 69 per cent. due to thorium-X and subsequent products.

This completes the series of thorium disintegration products as far as the emanation.

**Investigation of the Thorium Active Deposit.** The "active deposit" derived from the thorium emanation undergoes change, and the "excited activity" is the result of this change. This excited activity, when caused by *long* exposure of a body to the emanation, decays exponentially with a half-period of about eleven hours. Rutherford<sup>1</sup> made the remarkable observation, however, that the activity of the deposit obtained by a *short* exposure increased for several hours before decaying, but that the longer the exposure the shorter was the subsequent period of increase before decay set in. Rutherford<sup>2</sup> explained this phenomenon by supposing that the active deposit consists of two substances, *thorium-A* and *thorium-B*. Thorium-A was thought to be rayless in its change into thorium-B, whilst thorium-B was supposed to emit all three kinds of rays in changing into a further, almost inactive, product, *thorium-C*. Thus the observed activity of the deposit was due to thorium-B, the development of activity after short exposure was due to the generation of active thorium-B from inactive thorium-A; and the shortness of the period of increase before decay after longer exposure was due to the lateness in the life history of thorium-B at which the observation of activity was commenced. These conclusions, though right in principle, were subsequently modified in detail, because the product at first called thorium-A was discovered to be not the first member of the active deposit. When this new member was discovered it became thorium-A, the former thorium-A being called thorium-B, and so on. Further progress was achieved through the measurement of ionisation range, *i.e.* the distance the  $\alpha$ -ray can penetrate a gas as revealed by the ionisation of the gas. Hahn<sup>3</sup> applied this method of investigation to the thorium active deposit, and observed that two types of  $\alpha$ -radiation are emitted by the deposit, whose ranges were said to be 8.6 cm. and 4.7 cm.; so he concluded that the radiations are derived from two successive products, thorium-B and thorium-C. Which was the prior radiation, however, was not discovered, and it appeared that the change of thorium-B into thorium-C must be very rapid, since the two types always occur together in the same relative

<sup>1</sup> Rutherford *Physikal. Zetsch.*, 1902, 3, 254; *Phil. Mag.*, 1903, [vi], 5, 95.

<sup>2</sup> Rutherford *Phil. Trans.*, 1904, A, 204, 169.

<sup>3</sup> Hahn, *Phil. Mag.*, 1906 [vi], 11, 792; 12, 82.

proportions. In the same year that these results were obtained (1906) von Lorch<sup>1</sup> stated that thorium-A, formerly regarded as rayless, emits a small amount of  $\alpha$  radiation of penetrating character. This conclusion, however, appears not to have been maintained, for in 1909 it was recognised that thorium-A (half-period 10.6 hours) gives no  $\alpha$  particles, but that the product thorium-B and -C (half-period 60.4 minutes) gives two  $\alpha$ -particles of different ranges.<sup>2</sup>

Further progress was made through the introduction of a new method of investigation—the *method of recoil*. According to the principle of equality of momentum (Newton's third law of motion) the expulsion of an  $\alpha$ -particle from an atom with a certain velocity results in the recoil of the remaining portion of the atom with a velocity related to that of the  $\alpha$  particle inversely as the relation of two masses. This velocity confers a nascent volatility upon the atomic residue, and advantage is taken of this volatility to isolate a product that would otherwise escape notice. This method applied to the thorium active deposit yielded a new product, called thorium-D, which gives only  $\beta$ - and  $\gamma$ -rays and decays exponentially with a half-period estimated to be 3.4 minutes. Thorium-D is the last known member of the series, but further discoveries with regard to the intervening products have yet to be recorded.

It has already been stated that another product has been discovered in the emanation and what was formerly called thorium-A.

Bronson<sup>3</sup> in 1908 obtained evidence that an atom of the thorium emanation probably emits, in all, four  $\alpha$ -particles, and this conclusion was confirmed by Geiger and Marsden<sup>4</sup> in 1910, who observed the scintillations produced by the impact of the particle upon a zinc-sulphide screen, and concluded that the four  $\alpha$ -particles were not expelled simultaneously. Moreover, numerous cases of double scintillations separated by a very short time interval were observed in similar parts of the field, and thence the conclusion was drawn that at least one short-lived product exists with a half-time period of 0.11 second. The subject was further investigated by Rutherford and Geiger<sup>5</sup> who showed that if a rod coated with zinc sulphide is immersed in the thorium emanation and charged negatively it glows in the dark, but that the glow suddenly dies out when the rod is discharged. This is taken to show that a positively charged product of the thorium emanation exists, which is attracted to the negative electrode and there becomes visible by causing zinc sulphide to phosphoresce. For the glow to continue, however, the attraction must be continuous, because the product itself is very short-lived.

The rapid decay of this product was also shown by passing a negatively charged endless wire axially through a cylinder closed with pierced bronze stoppers and containing the thorium emanation, and driving the wire by means of a motor. The activity on the wire, examined by means of a zinc sulphide screen, was observed to decay at a little distance from the cylinder and the more slowly the wire was driven the shorter was the distance along it through which the

<sup>1</sup> Von Lorch, *Physikal. Zeitsch.*, 1906, 7, 913.

<sup>2</sup> Soddy, *Ann. Report Chem. Soc.*, 1909, p. 247.

<sup>3</sup> Hahn and Meitner, *Ber. Physik. Ges.*, 1909, 11, 55.

<sup>4</sup> Bronson, *Phil. Mag.*, 1908, [vol. 16, 291.

<sup>5</sup> Geiger and Marsden, *Physikal. Zeitsch.*, 1910, 11, 7.

<sup>6</sup> Rutherford and Geiger, *Phil. Mag.*, 1906, [vol. 12, 621.

activity persisted. The period of half-change of this short-lived product, now called **thorium-A**, is 0.11 second; and the product itself is analogous in properties to radium-A, a short-lived,  $\alpha$ -ray giving product whose existence was early observed. It will be remembered that the original thorium-A, having a half-change period of 10.6 hours, was thought to be rayless. This is now **thorium-B**, and is known to produce  $\beta$ -rays of feeble penetrating power. This thorium-B may be separated from thorium-C by taking advantage of its superior volatility.<sup>1</sup> Thus, if a wire, on which the active deposit is kept at red heat for a short time, thorium-B sublimes and is deposited on an adjacent surface. The consequence of this sublimation is that whilst there is no immediate effect on the activity of the wire, this activity decays more rapidly than before, because no thorium-B remains upon the wire to produce thorium-C, the store of which is the sooner exhausted. The sublimate which at first appears inactive develops an activity which reaches a maximum in four hours, and then decays with a half-period of 10.6 hours; this proves it to be thorium-B.

Thus far the elucidation of the nature of the thorium active deposit has yielded the following result

Emanation ( $\alpha$ -rays) — thorium-A ( $\alpha$ -rays) — thorium-B (soft  $\beta$ -rays) — thorium-C.

**Thorium-C and Branching Disintegration.** When the thorium active deposit is dissolved in acid, thorium-C can be removed from the solution by adsorption with animal charcoal or by shaking the solution with finely divided nickel, thorium-B remaining in the solution. Or if the active deposit upon a wire is heated for a few minutes to 1000°C all the thorium-B is volatilised, leaving some thorium-C upon the wire.

If thorium-C is regarded as a single substance it appears to emit  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays; but slight differences have been observed in the qualities of each kind of ray. Thus on closer examination thorium-C appears to emit two kinds of  $\alpha$ -rays, and the more penetrating part of the  $\beta$ -rays, but no  $\gamma$ -rays, which come from a subsequent product, thorium-D. So at the outset there is evidence of complexity in the case of thorium-C.

The  $\alpha$ -particles emitted by thorium-C are of two degrees of penetrating power, thus it appears to undergo *dual disintegration*. For every 100  $\alpha$ -particles given by the thorium emanation thorium-C produces, directly or indirectly, 35 of 4.55 cm. range and 65 of 8.16 cm. range.<sup>2</sup>

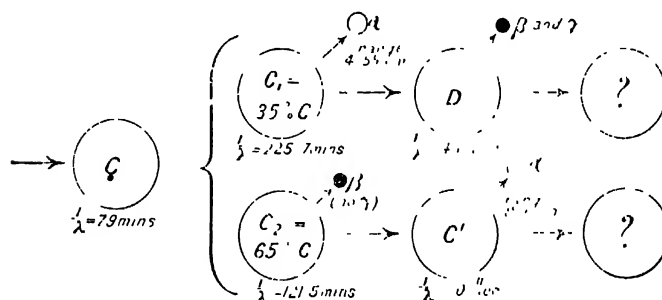
Thorium-C was at first thought to be homogeneous, yet it behaves as if it consisted of two kinds of matter, which have been styled thorium-C<sub>1</sub> and thorium-C<sub>2</sub>, for its atoms disintegrate<sup>3</sup> in two distinct ways. If thorium-C is homogeneous the following relations hold: The period of average life,  $\frac{1}{\lambda}$ , of thorium-C is 79 minutes; but  $\lambda = \lambda_1 + \lambda_2$ , where  $\lambda$  is the radioactive constant of thorium-C, and  $\lambda_1$  and  $\lambda_2$  are the corresponding constants of thorium-C<sub>1</sub> and thorium-C<sub>2</sub> respectively; and, according to the rates at which  $\alpha$ -particles are evolved,  $\lambda_1/\lambda_2 = 35/65$ ;

<sup>1</sup> Miss Slater, *Phil. Mag.*, 1905, [vi], 9, 628.

<sup>2</sup> Soddy, *Ann. Report Chem. Soc.*, 1912, p. 312.

<sup>3</sup> Marsden and Darwin, *Proc. Roy. Soc.*, 1912, A, 87, 17.

also the fraction  $\frac{\lambda_1}{\lambda_1 + \lambda_2}$  disintegrates according to the method of thorium-C<sub>1</sub> and the fraction  $\frac{\lambda_2}{\lambda_1 + \lambda_2}$  according to the method of thorium-C<sub>2</sub>. Further, since  $\frac{1}{\lambda_1 + \lambda_2} = \frac{1}{\lambda_1} = \frac{1}{\lambda_2} = 79$  minutes, and  $\frac{\lambda_1}{\lambda_1 + \lambda_2} = 35/65$ , it follows that  $\frac{1}{\lambda_1} = 225.7$  minutes and  $\frac{1}{\lambda_2} = 121.5$  minutes. Of the supposed homogeneous atoms of thorium-C, 35 per cent (thorium-C<sub>1</sub>) produce each a single particle in their disintegration, and the remaining 65 per cent (thorium-C<sub>2</sub>) each a mixed  $\beta$ -particle, unaccompanied by a  $\gamma$ -ray. Thus, while thorium-C<sub>1</sub> produces directly 35 per cent of the  $\alpha$ -particles of range 4.55 cm. derived from thorium C, and so passes into thorium-D, thorium-C<sub>2</sub> does not directly produce any  $\alpha$ -particles, but whilst itself producing  $\beta$ -particles gives rise to a short-lived ( $10^{-11}$  second)<sup>1</sup> product designated thorium C', whence the above-mentioned  $\alpha$ -particles of range 8.16 cm. (65 per cent) are evolved. These relationships are shown in the following diagram.



It is thus shown that all the  $\gamma$ -rays produced in the disintegration of the active thorium deposit come from thorium D. These  $\gamma$ -rays are the hardest or most penetrating known, but the  $\beta$ -rays which accompany them are less penetrating than those derived from thorium-C<sub>2</sub>, which may be described as hard. The mixed  $\beta$ -rays from thorium D and thorium-C<sub>1</sub> are half absorbed in 0.11 mm. of aluminium foil, the softer  $\beta$ -rays from thorium-D in 0.32 mm., and the harder  $\beta$ -rays from thorium-C<sub>2</sub> in 0.18 mm. (calculated).

It may be remarked that in one branch from thorium-C  $\beta$ -(with  $\gamma$ -) rays follow  $\alpha$ -rays, and in the other branch  $\beta$ -(without  $\gamma$ -) rays precede  $\alpha$ -rays.

This is the first known example of penetrating  $\beta$ -rays, unaccompanied by  $\gamma$ -rays.

According to Meitner,<sup>2</sup> however, 'thorium C' is not homogeneous,

<sup>1</sup> This extraordinarily short period of average life is calculated from the range (8.16 cm.) by means of the Geiger-Nuttall relation (Geiger and Nuttall, *Phil. Mag.*, 1911, [vi], 22, 619; 1912, 23, 439, 24, 647), which states that the shorter the period the greater the velocity of the expelled  $\alpha$ -particle.

<sup>2</sup> Meitner, *Physikal. Zeitsch.*, 1912, 13, 623; see also von Hevesy, *Phil. Mag.*, 1912, [vi], 23, 628.

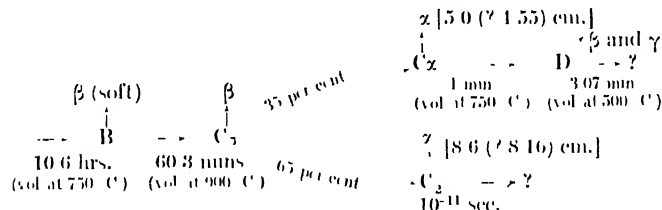


but consists of two kinds of atoms producing two kinds of  $\alpha$ -radiation. The evidence for this view is in the fact that when nickel plates are immersed in a solution of thorium-C containing stannous chloride the deposit consists of the 65 per cent. portion, the other portion being left in solution. Although these results were criticised,<sup>1</sup> it has been shown by Barratt and Wood<sup>2</sup> that thorium-C consists of two constituents which may be separated by taking advantage of their different degrees of volatility.

When the thorium active deposit on platinum or quartz plates is heated for fifteen minutes in an electric furnace whose temperature is carefully regulated, the 35 per cent. portion of thorium-C giving the  $\alpha$ -activity begins to volatilise at 750° C., while the 65 per cent. portion becomes volatile at 900° C. This shows that thorium-C is not homogeneous, as was previously supposed, but that the constituent giving first  $\alpha$ -rays and then  $\beta$ -rays is distinct from that which gives first  $\beta$ -rays and then  $\alpha$ -rays.

Thorium-D is volatile at about 500° C., a lower temperature than that at which thorium-C or its products are volatile. Therefore, if the preparation is heated between 500° C. and 900° C. so as to volatilise thorium-D with its characteristic  $\beta$ -radiation,  $\beta$ -rays begin to appear after cooling, owing to the reaccumulation of thorium-D, derived from thorium-C which was not volatilised. But if the preparation is heated above 900° C., so as to volatilise thorium-C, no source of thorium-D remains, and so its  $\beta$ -radiation does not reappear.

In order to express these results the disintegration scheme has been modified as follows:



Thorium-C (or C<sub>2</sub>) of half-change period 60.3 minutes (instead of 79 minutes) is now supposed to branch, giving rise to two products, the first of which, C<sub>3</sub>, with half-change period of about 1 minute (calculated from the Geiger-Nuttall relation), has not previously been recognised. It is this which was volatilised in the electric furnace at 750° C. and is the parent of thorium-D.

In the other branch the original C<sub>2</sub> disappears, since its  $\beta$ -rays are given off by C<sub>3</sub>, and the former C' is promoted to the place of C<sub>2</sub>. It will be observed that C<sub>3</sub> and C<sub>2</sub> are so called because they give rise to  $\beta$ - and  $\alpha$ -rays respectively.

**Thorium-D**, which under ordinary conditions begins to volatilise at 520° C., is altered by treatment with hydrochloric acid, so that it begins to volatilise at 270° C. and is completely volatilised below 500° C. It is more soluble in acids and more volatile than any other thorium

<sup>1</sup> Marsden and Wilson, *Phil. Mag.*, 1913, [vi], 26, 354.

<sup>2</sup> Barratt and Wood, *Proc. Physical Soc.*, 1914, 26, 248.





products,<sup>1</sup> and is completely volatilised by heating a wire on which it is deposited for 30 seconds in the Bunsen flame. It has a half-change period of 3.07 minutes; moreover, it is the last known member of the series and its decay appears to be complete, there being no feeble residual activity as there is in the case of radium. If the ultimate product, sometimes known as thorium F, is not emitted in table, it must possess a life-period of at least two million years.<sup>2</sup>

The final disintegration product in both branches should be isotopic (*vide infra*) with lead and have the same atomic weight as it.

Several other matters connected with the radioactivity of thorium, not included in the above historical study, may here be noticed.

*Isotopy in the Thorium Series.*—The idea of isotopy arose from a study of radioactive changes with reference to the Periodic Law,<sup>3</sup> and it may be briefly stated here that the loss of an  $\alpha$  particle, with four units of atomic weight, transfers an element back into the previous group but one in the periodic table whilst the loss of a  $\beta$  particle without alteration of atomic weight carries the element one stage forward into the next group of the table.<sup>4</sup> Consequently by successive losses of  $\alpha$ - and  $\beta$ -particles a disintegrating element may pass backwards and forwards, through different groups of the periodic system. It therefore follows, that the radioactive element in the course of its history will coincide in position with various other elements occupying well-recognised places in the system, although its atomic weight will not generally be identical with that of the element with which it coincides. Elements which thus occupy the same place in the periodic table are found to be chemically non-separable and identical and are said to be *isotopic* and to constitute a group of *isotopes*.

The isotopes of the thorium disintegration products are as follow; the Roman numerals indicate the periodic group to which the isotopes belong:

- I A Thorium is isotopic with mannum-X, ionium, radiothorium, radioactinium.
- II A Mesothorium-1 is isotopic with thorium-X, actinium-X, radium.<sup>5</sup>
- III A Mesothorium-2 is isotopic with actinium.
- IV A Radiothorium is isotopic with thorium, ionium, mannum-X, radioactinium.
- II A Thorium-X is isotopic with mesothorium-1, actinium-X, radium.
- O Thorium-emanation is isotopic with radium and actinium emanations.
- VI B Thorium-A is isotopic with radium-A, polonium, thorium-C.
- IV B Thorium-B is isotopic with radium-B, actinium-B, radium-D, lead.<sup>6</sup>

<sup>1</sup> Von Lorch and von Wuthenow, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, [16, a], 118, 1575.

<sup>2</sup> Von Lorch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1907, [16, a], 116, 1113.

<sup>3</sup> Fick, Soddy, *The Chemistry of the Radio Elements*, p. 111 (Longmans and Co., 1911).

<sup>4</sup> Fick, *Trans. Chem. Soc.*, 1913, 103, 381, 1032; Russell, *Chem. News*, 1913, 107, 49; von Hevesy, *Physikal. Zeitsch.*, 1913, 14, 49; *Fajans, ibid.*, 1913, 14, 131, 136.

<sup>5</sup> Soddy, *Chem. News*, 1913, 107, 97; Jahn, *Elektronik*, 1913, 10, 188.

<sup>6</sup> Mackwald, *Ber.*, 1910, 43, 3420; Soddy, *Trans. Chem. Soc.*, 1911, 99, 72.

<sup>7</sup> Fick, *Trans. Chem. Soc.*, 1913, 103, 381, 1052.

V B. Thorium-C $\beta$  is isotopic with radium-C, actinium-C, radium-E, bismuth.<sup>1</sup>

III B. Thorium-D is isotopic with actinium-D, thallium.<sup>1</sup>

Since all isotopic elements are chemically identical, it follows that the number of new elements brought to light by the science of radio-activity is fewer than would at first sight appear. The new elements in the above list are radium, polonium, and the emanation. The remarkable conclusion to be drawn from these studies is that electrical content and not mass determines the physical and chemical properties of an element, since isotopes have different atomic weights but identical properties.

*The Preparation and Utility of Mesothorium-1.* The isotopy of mesothorium-1 with radium suggests that preparations of the former substance may be used as a substitute for radium preparations. Moreover, enormous quantities of thorium minerals are now worked up in connection with the gas-mantle industry; and consequently mesothorium-1, which is a by-product of this industry, has recently assumed commercial importance. Mesothorium-1 is separated from the thorium derived from monazite sand by adding a small quantity of a barium compound to the sand previous to or during its treatment with concentrated sulphuric acid. When the product is poured into water the whole of the mesothorium-1 is obtained, together with barium sulphate, in the lighter portion of the residue, because this substance, being isotopic with radium in Group II A, forms an exceedingly insoluble sulphate.<sup>2</sup>

Further, on account of the chemical identity of mesothorium-1 with radium, the radium separated from pitchblende and other uranium minerals necessarily contains all the mesothorium in the mineral; and, conversely, mesothorium preparations will contain any radium present in their source. The presence of mesothorium-1 in radium may be detected by measuring the absorption coefficient for  $\gamma$ -rays, since the  $\gamma$ -rays of mesothorium-1 have rather less penetrating power than those of radium.<sup>3</sup>

According to Hahn<sup>4</sup> the monazite sand from which mesothorium is prepared contains 0.3 per cent. of uranium, and 4 to 5 per cent. thorium; and of the activity of the preparation 75 per cent. is due to mesothorium and 25 per cent. to radium. Mesothorium, however, is characterised by a developing activity which reaches its maximum in 3.2 years and then begins to decay; after ten years this activity is still greater than when the substance was first prepared, and after twenty years is about half as great. When freed from inactive material the product is four times as active as a pure radium compound, and contains 1 per cent. of mesothorium to 99 per cent. of radium. It may be seen, therefore, that although less permanent than radium, mesothorium preparations are a valuable substitute for pure radium compounds.

*The complete series of thorium disintegration products* is shown in the accompanying chart, in which the times are periods of average life.<sup>5</sup>

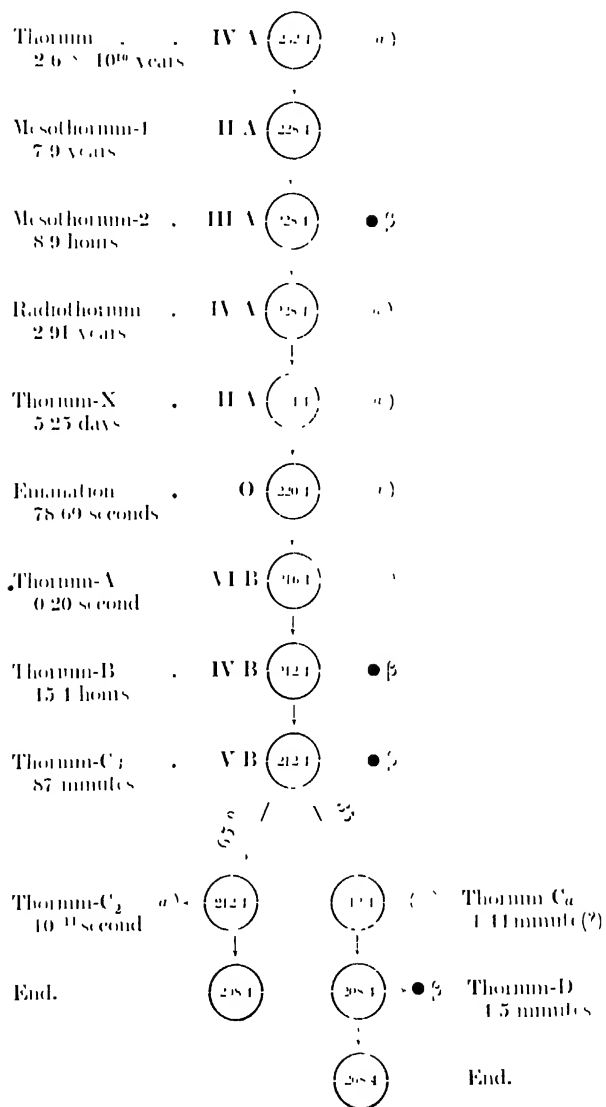
<sup>1</sup> Fleck, *Trans. Chem. Soc.*, 1913, 103, 381, 1052.

<sup>2</sup> Soddy, *Trans. Chem. Soc.*, 1911, 99, 72.

<sup>3</sup> Russell and Soddy, *Phil. Mag.*, 1911, [vi], 21, 130.

<sup>4</sup> Hahn, *Chem. Zeit.*, 1911, 35, 815.

<sup>5</sup> Period of average life = period of half-change  $\times 1.44$ .



## CHAPTER VII GERMANIUM AND ITS COMPOUNDS

### GERMANIUM

Symbol, Ge. Atomic weight, 72.5 (O = 16)

**Occurrence.** Germanium is a rare element occurring in very few minerals. The chief of these is *argyrodite*, found at Freiberg in Saxony, with which *caufeldite* from Bohemia appears to be nearly identical. Winkler,<sup>1</sup> who first investigated argyrodite and discovered germanium in it, attributed to the mineral the formula  $3\text{Ag}_2\text{S} \cdot \text{GeS}_2$ , but Penfield<sup>2</sup> and Kolbeck<sup>3</sup> have shown that it is more accurately represented by the formula  $4\text{Ag}_2\text{S} \cdot \text{GeS}_2$ , as the following figures show.

	S	Ag	Ge	Hg	Pb, Zn and Residue	Total
Argyrodite	17.13	74.72	6.93	0.31	0.88	99.97
Caufeldite	17.01	76.05	6.55	-	0.12	100.06
$4\text{Ag}_2\text{S} \cdot \text{GeS}_2$	17.06	76.52	6.12	-	-	100.00
$3\text{Ag}_2\text{S} \cdot \text{GeS}_2$	18.21	73.56	8.23	-	-	100.00

Germanium is also found in *Mexican blende*, in *euxenite*<sup>4</sup> to the extent of 0.1 per cent., also in *samaraskite*, *tantalite*, *frigusoulite*, *mobite* and *gadolinite*,<sup>5</sup> but argyrodite remains the chief source of the element.

**Discovery.**—Winkler<sup>6</sup> analysed argyrodite, but his first analytical still left added up to only 93-94 per cent. As in the analogous case of tellurium, the deficiency was subsequently accounted for by the discovery of the new element, isolated by Winkler in 1886, and called by him *germanium*. Winkler at first thought that this new element would fill the supposed gap between antimony and bismuth, but soon recognised that it was quadrivalent and identical with Mendeléeff's *ekasilicon*, one of the elements predicted by means of the Periodic Law.

<sup>1</sup> *Th.*  
accompanied, *Ber.*, 1886, 19, 210  
<sup>2</sup> *ibid.*, *Amer. J. Sci.*, 1893, [iii], 46, 107, see also Goldschmidt, *Zeitsch. Krist.*

<sup>3</sup> 518  
<sup>4</sup> *Chem. Zentr.*, 1908, ii, 346, from *Zentr. f. Min. u. Geol.*, 1908, 331

<sup>5</sup> *ibid.*, 1888, 21, 131

<sup>6</sup> *ibid.*, *Chem. Zentr.*, 1895, ii, 977

<sup>7</sup> *Petrog.*, 1896, 19, 210

The predicted and realised properties of germanium and its compounds are here shown side by side :

GERMANIUM.	GERMANIUM
Atomic weight 72.	Atomic weight 72.5.
Density 5.5.	Density 5.469.
<i>Oxide</i> , $\text{EsO}_2$ , density 4.7.	<i>Oxide</i> , $\text{GeO}_2$ , density 4.703.
<i>Chloride</i> , $\text{EsCl}_4$ , liquid, B.P. slightly below $100^\circ\text{C}$ , density 1.9.	<i>Chloride</i> , $\text{GeCl}_4$ , liquid, B.P. $86^\circ\text{C}$ , density 1.887.
<i>Ethide</i> , $\text{Es}(\text{C}_2\text{H}_5)_4$ , liquid, B.P. $160^\circ\text{C}$ , density 0.96.	<i>Ethide</i> , $\text{Ge}(\text{C}_2\text{H}_5)_4$ , liquid, B.P. $160^\circ\text{C}$ , slightly lighter than water.
<i>Fluoride</i> , $\text{EsF}_4$ , not gaseous.	<i>Fluoride</i> , $\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ , solid.

**Preparation.** The metal was prepared by Winkler<sup>1</sup> from argyrodite in the following way. Three parts of the finely powdered mineral were fused at a bright red heat with six parts of potassium nitrate and three parts of potassium carbonate. The alkali germanate thus formed was separated from the metallic silver by extraction with water, and the solution was evaporated with sulphuric acid till nitric acid ceased to be evolved. Most of the germanium then separated as dioxide, and the remainder was precipitated as sulphide, which was roasted and converted finally into oxide by treatment with nitric acid. This oxide was further purified by being converted into the insoluble germanfluoride,  $\text{K}_2\text{GeF}_6$ , and thence into sulphide,  $\text{GeS}_2$ , by fusion with potash and sulphur, the sulphide was afterwards decomposed by sulphuric acid, and so reconverted into oxide. The oxide was then reduced by heating it with carbon and the resulting metal after being washed with water, was purified by fusion with borax. The metal may also be obtained from potassium germanfluoride,  $\text{K}_2\text{GeF}_6$ , by reduction in a stream of hydrogen or with sodium, or the dioxide can be reduced by hydrogen or magnesium. Urban, Blondel, and Obiedoff have extracted 5 grams of pure germanium from 550 kilograms of a Mexican blende.<sup>2</sup>

**Properties.** Germanium is a greyish white, brittle, lustrous metal which crystallises in the regular system, its density at  $20^\circ\text{C}$ . is 5.469, and it melts at  $958 \pm 5^\circ\text{C}$ . and when saturated with oxide at  $916 \pm 5^\circ\text{C}$ .<sup>3</sup> According to Winkler<sup>4</sup> the boiling-point of germanium is not much above its melting-point. Meyer and Mensching,<sup>5</sup> however, have found little sign of volatility when the metal is heated to  $1350^\circ\text{C}$ . in an atmosphere of hydrogen or nitrogen, but in presence of some oxide, vapour is observed from  $750^\circ\text{C}$ . onwards.<sup>6</sup> The specific heat was found by Nilson and Pettersson<sup>7</sup> to vary somewhat with temperature as follows.

Temperature $^\circ\text{C}$	0-100	0-211	0-301.5	0-440
Specific heat	0.0737	0.0773	0.0768	0.0757
Atomic heat	5.34	5.59	5.55	5.17

<sup>1</sup> Winkler, *J. prakt. Chem.*, 1887, 36, 111.

<sup>2</sup> Urban, Blondel, and Obiedoff, *Compt. rend.*, 1910, 150, 1778.

<sup>3</sup> Biltz, *Zeitsch. anorg. Chem.*, 1911, 72, 313.

<sup>4</sup> Winkler, *J. prakt. Chem.*, 1886, 31, 177.

<sup>5</sup> V. Meyer and Mensching, *Ber.*, 1887, 20, 197.

<sup>6</sup> Nilson and Pettersson, *Zeitsch. physikal. Chem.*, 1887, 1, 87.



The most intense lines in the spectrum of germanium are as follows<sup>1</sup>:

Arc : 2592.61, 2651.28, 2651.69, 2691.45, 2709.70, 2754.69, 3039.22, 3269.62

Spark : 2592.65, 2651.29, 2651.69, 2709.69, 2754.68, 3039.20, 4179.20, 4226.76.

Germanium dissolves in aqua regia, but not in hydrochloric acid, whilst towards nitric acid it behaves like tin, being converted into the dioxide. It is oxidised at high temperature, and combines directly with the halogens.

#### ATOMIC WEIGHT OF GERMANIUM

The order of magnitude of the atomic weight of germanium has never been in question, since before the discovery of this metal a space with a corresponding atomic weight was allotted to it by Mendeléeff in his Periodic Table. "We must expect the discovery of many yet unknown elements," said Mendeléeff in his *Faraday Lecture* in 1889; "for example, elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75."<sup>2</sup> The elements referred to are gallium, Ga (atomic weight = 69.6), and germanium, Ge (atomic weight = 72.5). That the atomic weight of germanium is about 72 is shown as follows. The specific heat<sup>3</sup> of the metal between 0° C. and 110° C. is 0.0737-0.0757, which gives an atomic heat of 5.31-5.17 if the atomic weight is 72.5. This value is further supported by the isomorphism<sup>4</sup> of potassium germanifluoride,  $K_2GeF_6$ , with the corresponding siliconfluoride,  $K_2SiF_6$ . The atomic weight of germanium was determined by Winkler<sup>5</sup> in 1886, and no more recent determination has been made. A weighed quantity of purified germanium tetrachloride was added to excess of standardised silver nitrate solution, and the silver remaining in solution after precipitation of the chloride was titrated with ammonium thiocyanate solution, according to Volhard's method. As the mean of four closely agreeing results, germanium tetrachloride,  $GeCl_4$ , was found to contain 66.173 per cent. of chlorine; and from this percentage the atomic weight  $Ge = 72.32 \pm 0.015$  was calculated on the basis  $H = 1$ ,  $O = 15.96$ ,  $Ag = 107.66$ . This value was recalculated by Clarke<sup>6</sup> in 1910 on the basis  $O = 16.000$ ,  $Ag = 107.880$  and  $Cl = 35.458$ , so that  $Ge = 72.501$ .

The value adopted by the International Atomic Weights Committee for 1917 is **Ge = 72.5**.

<sup>1</sup> Exner and Haschek, *Die Spektren der Elemente bei normaler Druck* (Leipzig and Wien, 1911).

<sup>2</sup> Mendeléeff, *Trans. Chem. Soc.*, 1889, 55, 635.

<sup>3</sup> Nilson and Pettersson, *Zetsch. physikal. Chem.*, 1887, 1, 87.

<sup>4</sup> The argument is precisely the same as that detailed under titanium, p. 235.

<sup>5</sup> Winkler, *J. prakt. Chem.*, 1886, 34, 177.

<sup>6</sup> Clarke, *A Recalculation of the Atomic Weights*, Smithsonian Collections, Washington, 1910, vol. iv., No. 3, p. 286.

## COMPOUNDS OF GERMANIUM

Germanium resembles tin in behaving both as a bivalent and a quadrivalent element. Both oxides  $\text{GeO}$  and  $\text{GeO}_2$  are lightly soluble in water, forming faintly acid solutions. They also dissolve in acids, but form no oxy-salts. The sulphides are well known and they resemble those of tin in forming thio-salts with alkali sulphides. Germanium resembles silicon in forming the hydride  $\text{GeH}_4$  and the chloroform  $\text{GeHCl}_3$ , whilst the complex fluoride  $\text{F}_3\text{GeF}_6$  resembles potassium silicofluoride,  $\text{K}_2\text{SiF}_6$ . The existence of germanium tetra-ethyl,  $\text{Ge}(\text{C}_2\text{H}_5)_4$ , is in accord with the position the element occupies at the head of Sub-group IV B in the Periodic Table.

The following are the compounds of germanium:

	Ge II	Ge IV
Hydride		$\text{GeH}_4$
Ethide or tetra-ethyl		$\text{Ge}(\text{C}_2\text{H}_5)_4$
Chloroform		$\text{GeHCl}_3$
Halides	$\text{GeF}_2, \text{GeCl}_2$	$\text{GeF}_4, \text{GeCl}_4, \text{GeBr}_4, \text{GeI}_4, \text{H}_2\text{GeF}_6$
Oxychloride		$\text{GeOCl}_2$
Oxides	$\text{GeO}$	$\text{GeO}_2$
Hydroxides	$\text{Ge}(\text{OH})_2$ , or $\text{HGeO}_2\text{OH}$	$\text{Ge}(\text{OH})_4(?)$ , $\text{Ge}(\text{OH})_2(?)$
Sulphides	$\text{GeS}$	$\text{GeS}_2$

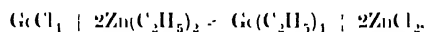
**Germanium Hydride,  $\text{GeH}_4$**  In forming a gas, the hydride germanium relates itself to silicon and the non-metals rather than to the metals.

This compound was not obtained by Winkler, but was first prepared by Vogelen<sup>1</sup> by reducing germanium chloride with sodium amalgam, or with nascent hydrogen generated as in Marsh's test. The hydrogen, mixed with germanium hydride, burns with a bluish red flame and deposits a mirror on a cold surface, which is soluble in sodium hypochlorite solution. The deposit obtained by heating the tube through which the gas passes is red in transmitted and green in reflected light. When the gas is passed into silver nitrate solution, germanium-silver is precipitated, which is converted into germanic oxide,  $\text{GeO}$ , by concentrated nitric acid. By the analysis of this compound, as well as by passing the hydride over finely divided sulphur in a strong light and comparing the amounts of germanium and hydrogen sulphide formed, the discoverer attempted to decide between the formulae  $\text{GeH}_2(\text{Ge}_2\text{H}_7)$  and  $\text{GeH}_4$ . The analytical results were not satisfactory owing to the small amount of material available, but they sufficed to show that the hydride is very probably  $\text{GeH}_4$ .

**Germanium Tetra-ethyl,  $\text{Ge}(\text{C}_2\text{H}_5)_4$**  The existence of this compound, the properties of which were foretold by Mendeléeff, shows that

<sup>1</sup> *Vogel's Zetschnung of Chem.* 1902, 30, 325.

germanium shares with other metals of the B subgroups the ability to form volatile organo-metallic compounds. It is formed by the interaction of germanic chloride and zinc ethyl in an atmosphere of carbon dioxide:



is separated from the zinc chloride by water, extracted with ether, dried and distilled.

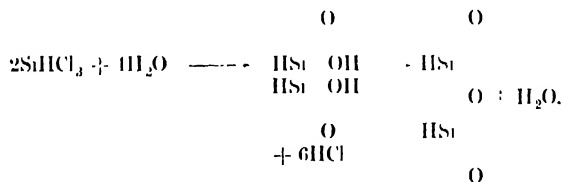
Germanium ethyl is a colourless liquid having a feeble odour like that of leeks; it is immiscible with, and lighter than, water and boils at  $160^\circ\text{C}$ . Its vapour density<sup>1</sup> at  $230^\circ\text{C}$  is 119 ( $\text{H} = 1$ ), which corresponds to a molecular weight of 238. Since the molecular weight corresponding to the formula  $\text{Ge}(\text{C}_2\text{H}_5)_4$  is 188, the molecules are probably associated in the state of vapour. The vapour burns with a yellowish red flame and forms an explosive mixture with oxygen.

**Germanium Chloroform,  $\text{GeHCl}_3$** —This compound, like the hydride  $\text{GeH}_4$ , connects germanium with the non-metals carbon and silicon. Indeed  $\text{GeHCl}_3$  closely resembles  $\text{SiHCl}_3$  in chemical properties.

Germanium chloroform is formed as a vapour, condensable in ice to a volatile liquid, when hydrogen chloride gas is passed over slightly heated powdered germanium. There is formed at the same time, owing to the presence of a trace of water a certain quantity of the oxychloride  $\text{GeOCl}_2$ , which it is difficult to remove from the chloroform. Germanium chloroform is a colourless liquid boiling at  $72^\circ\text{C}$ , which becomes turbid on exposure to air owing to the formation of the oxychloride, and is decomposed by water, with separation of germanous hydroxide, thus:



This manner of decomposition does not at first appear to be analogous to that of silicon chloroform, which reacts thus with water



but if  $\text{Ge}(\text{OH})_2$  is regarded as an analogue of formic acid, having the constitution  $\text{HGe}(\text{OOH})$ , the analogy becomes apparent.

The vapour density of  $\text{GeHCl}_3$  has been found to be 79.9<sup>1</sup> ( $\text{H} = 1$ ); since the theoretical value is 89.4 there appears to be some dissociation

#### GERMANIUM HALIDES

**Germanous Fluoride,  $\text{GeF}_2$** , is formed as a dark-coloured mass, mixed with metallic germanium, when potassium germanofluoride,  $\text{K}_2\text{GeF}_6$ , is heated in a current of hydrogen.<sup>2</sup> The presence of the lower fluoride is

<sup>1</sup> Meyer and Mensching, *Ber.*, 1887, 20, 497

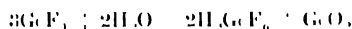
<sup>2</sup> Winkler, *J. prakt. Chem.*, 1887, 36, 177

shown by the formation of the brown monosulphide,  $\text{GeS}$ , when hydrogen sulphide is passed through the aqueous extract of the product.

**Germanic Fluoride**,  $\text{GeF}_4$ , has not been obtained in a pure anhydrous state, but is probably formed when the crystallhydrate  $\text{GeF}_4 \cdot 3\text{H}_2\text{O}$  is heated in a stream of carbon dioxide, as well as when a mixture of germanic oxide, calcium fluoride, and sulphuric acid is distilled.

The hydrate  $\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ <sup>1</sup> is obtained in large crystals when a solution of the dioxide in aqueous hydrofluoric acid is evaporated over sulphuric acid. These crystals are hygroscopic and easily dissolve in water; the solution, however, suffers hydrolysis, so that glass is etched by the liberated hydrofluoric acid.

**Hydrofluogermanic Acid**,<sup>1</sup>  $\text{H}_2\text{GeF}_6$ , is formed in solution in an analogous way to  $\text{H}_2\text{SiF}_6$  etc. by passing the vapour of the tetrafluoride into water:



The reaction differs, however, from the analogous reaction of silicon tetrafluoride, because the hydrated germanic oxide formed remains in solution. The addition of potash to the solution produces potassium germanifluoride, while excess of ammonia precipitates the oxide.

**Potassium Germanifluoride** (*Fluogermanate*),  $\text{K}_2\text{GeF}_6$ , is obtained in the course of extraction of germanium from arsenicite. It is best prepared<sup>1</sup> by dissolving 2 parts of germanic oxide in 12 parts of a 20 per cent. solution of hydrofluoric acid and adding 3 parts of potassium chloride in concentrated solution. After first separating as a jelly the salt is eventually obtained in hexagonal crystals isomorphous with ammonium selenifluoride. According to Winkler 1 part of potassium germanifluoride dissolves in 171 parts of water at  $18^\circ \text{C}$ . and in 31 parts at  $100^\circ \text{C}$ .

**Germanous Chloride**,<sup>1</sup>  $\text{GeCl}_2$ , is formed when hydrogen chloride gas is passed over the heated monosulphide,  $\text{GeS}$ . It is a colourless liquid which fumes in the air and is decomposed by water with separation of the corresponding hydroxide; it consequently possesses no saline properties. Its solution in concentrated hydrochloric acid is a powerful reducing agent.

**Germanic Chloride**,  $\text{GeCl}_4$ , may be prepared<sup>1</sup> by the union of the elements, excess of chlorine being removed by shaking the product with mercury, or by distilling the metal or the disulphide<sup>1</sup> with mercuric chloride. It is a thin, colourless liquid, having a density of 1.887 at  $18^\circ \text{C}$ . and boiling at  $86^\circ \text{C}$ ; its critical temperature is  $276.9^\circ \text{C}$ . and critical pressure 38 atmospheres. It does not solidify at  $-80^\circ \text{C}$ ., its vapour density at  $301.5^\circ \text{C}$ . was found to be 7.43 and 7.46 (air = 1),<sup>2</sup> or 107.0 and 107.4 ( $\text{H} = 1$ ), theory for  $\text{GeCl}_4$  requiring 7.40 (air = 1) or 106.6 ( $\text{H} = 1$ ); it is slowly decomposed by water with separation of the hydrated dioxide, and is reduced to metal when its vapour, mixed with hydrogen, is passed through a red-hot tube.

**Germanium Oxychloride**,<sup>1</sup>  $\text{GeOCl}_2$ , is produced from germanium chloroform by oxidation when the latter substance is being prepared<sup>1</sup> by warming germanium in a current of hydrogen chloride gas. It is also formed when a fine stream of air or oxygen is led through the

<sup>1</sup> Winkler, *J. prakt. Chem.*, 1887, **36**, 177.

Winkler, *J. prakt. Chem.*, 1886, **34**, 177.

<sup>2</sup> Nilson and Pettersson, *Z. physikal. Chem.*, 1887, **1**, 87.

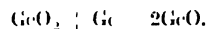
chloroform, and gradually separates therefrom as an oily liquid. Germanium oxychloride is a colourless liquid, less mobile than, and immiscible with, germanium chloroform; it does not fume in the air, and boils above  $100^{\circ}\text{C}$ .

**Germanic Bromide,**<sup>1</sup>  $\text{GeBr}_4$ , formed by the union of its elements, or by distilling a mixture of mercuric bromide and germanium, is a colourless liquid which solidifies at  $0^{\circ}\text{C}$  to a white crystalline mass. It fumes in the air and is hydrolysed by water, with separation of the hydrated dioxide.

**Germanic Iodide,**<sup>1</sup>  $\text{GeI}_4$ , is formed by the union of its elements, or by the interaction of germanic chloride and potassium iodide. It is an orange solid, which melts at  $114^{\circ}\text{C}$ , and boils above  $300^{\circ}\text{C}$ . Its vapour density at  $110^{\circ}\text{C}$  is 20.16 (air = 1) or 291.6 ( $\text{H}_2 = 1$ ), theory for  $\text{GeI}_4$  requiring 20.0 (air = 1) or 288.0 ( $\text{H}_2 = 1$ ). At a somewhat higher temperature the vapour begins to dissociate. The solid iodide deliquesces in the air and then gradually loses iodine and absorbs oxygen, so passing into the dioxide.

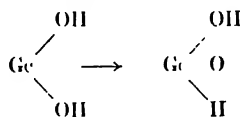
#### GERMANIUM AND THE OXYGEN GROUP

**Germanous Oxide,**  $\text{GeO}$ , is obtained by heating the hydroxide in an inert atmosphere, or by heating the dioxide with metallic germanium or with magnesium. Biltz,<sup>2</sup> however, could not bring about the reaction

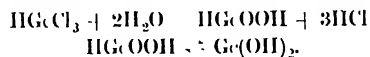


Germanous oxide is a greyish black powder which is volatile<sup>2</sup> and dissolves in hydrochloric acid, forming a solution of germanous chloride.

**Germanous Hydroxide,**  $\text{Ge}(\text{OH})_2$ , is formed as a yellow precipitate when alkali is added to a solution of the corresponding chloride. It is somewhat soluble in water, to which it imparts its yellow colour, and also in excess of alkali. If the hydroxide is heated with the liquid from which it has been precipitated it is reddened, and this is believed to be due to the tautomeric change:



the latter substance being the germanium analogue of formic acid. This idea is strengthened by the fact that germanous hydroxide is produced by the action of water on germanium chloroform.



Hantzsch<sup>3</sup> has shown that the hydroxides of zinc, aluminium, lead, tin (stannous), and germanium all behave as feeble acids whose strengths increase in the order given. This has been done by measuring the electric conductivities of alkaline solutions of these hydroxides and

<sup>1</sup> Winkler, *J. prakt. Chem.*, 1887, **36**, 177.

<sup>2</sup> Biltz, *Zeitsch. anorg. Chem.*, 1911, **72**, 313.

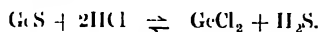
<sup>3</sup> Hantzsch, *Zeitsch. anorg. Chem.*, 1902, **30**, 289.

also by determining the rate of hydrolysis of ethyl acetate by such solutions, and comparing these effects with those produced by the alkali alone. Thus an indication is given of the extent to which the metallic hydroxide is combined with the alkali to form a salt, and so of the acidic strength of this hydroxide. Thence it appears that germanous hydroxide is a slightly weaker acid than acetic acid. It is to be noted that the acidic character of these hydroxides of germanium, tin, and lead depends upon the ability of the elements to become quadrivalent, and also that the acidic strengths diminish with increase of atomic weight.

**Germanic Oxide,  $\text{GeO}_2$**  The preparation of germanic oxide from argyrodite has already been described under the metal. This oxide may also be obtained by burning the metal, by oxidising the sulphide by nitric or sulphuric acid or by roasting, and by decomposing the chloride with water and igniting the product.

Germanium dioxide is a dense white powder, having a density <sup>1</sup> of 4.703 at 18° C.; it can be melted to a clear liquid, but is not volatile at 1025° C.<sup>2</sup> It is somewhat soluble in water, 1 part dissolving in 247.1 parts of water at 20° C. and in 95.3 parts at 100° C.; the solution reacts acid, and from it on evaporation the anhydrous oxide separates in microscopic rhombic crystals.<sup>3</sup> The ignited oxide forms with water an emulsion which becomes clear on heating owing to the formation of a colloidal solution. Germanium dioxide dissolves both in acids and alkalis; in the former case germanic salts appear to be produced in solution, in the latter alkali germanates. Carbon dioxide precipitates colloidal hydrated germanic oxide from alkali solution.<sup>4</sup> Neither of the hydroxides  $\text{GeO}(\text{OH})_2$  or  $\text{Ge}(\text{OH})_4$  is definitely known.

**Germanous Sulphide,  $\text{GeS}$** , the best characterised germanous compound, may be prepared in the dry or wet way. In the dry way it is produced by heating a mixture of the disulphide and metallic germanium in a current of carbon dioxide, or by igniting the disulphide in a stream of hydrogen. In the latter case reduction may proceed as far as the metal. In the wet way the sulphide is obtained by precipitating a germanous solution with hydrogen sulphide. Precipitated, amorphous germanous sulphide is brownish red, but when this compound is prepared in the dry way it is obtained in thin greyish black, metallic looking plates, which are rhombic or monoclinic and appear red by transmitted light;<sup>5</sup> it melts to a dark-coloured liquid and can be vaporised without decomposition, the vapour density<sup>6</sup> at 1100° C. being 3.51 (air = 1) or 51.0 ( $\text{H}_2$  = 1), theory for  $\text{GeS}$  requiring 3.60 (air = 1) or 51.8 ( $\text{H}_2$  = 1). This sulphide is slightly soluble in water, and dissolves in concentrated hydrochloric acid, forming a solution from which it is reprecipitated by hydrogen sulphide, thus:



It also dissolves in alkalis and is precipitated again by acid; with yellow ammonium sulphide it forms a thio-salt of  $\text{GeS}_2$ . Thus  $\text{GeS}$

<sup>1</sup> Nilson and Pettersson, *Zeitsch. physikal. Chem.*, 1887, 1, 87.

<sup>2</sup> Biltz, *Zeitsch. anorg. Chem.*, 1911, 72, 313.

<sup>3</sup> Haushofer, *Sitzungen Akad. Wiss. München*, 1887, 1, 133, see also *Ber.*, 1887, 20, Ref. 660.

<sup>4</sup> Van Bemmelen, *Rec. Trav. chim.*, 1887, 6, 205; see also *Ber.*, 1887, 20, Ref. 541.

<sup>5</sup> Kriess, *Ber.*, 1888, 21, 131.

<sup>6</sup> Nilson and Pettersson, *ibid.*

resembles SnS in chemical properties, though it is probably more acidic than the latter sulphide. When the precipitated sulphide is washed it shows a tendency to pass into the colloidal state.

**Germanic Sulphide,  $\text{GeS}_2$ ,** probably occurs naturally in argyrodite. It is obtained as a voluminous white precipitate by passing hydrogen sulphide through a solution of germanic oxide, or by adding mineral acid to a solution of germanous sulphide,  $\text{GeS}$ , in yellow ammonium sulphide. Weak organic acids, such as acetic acid, do not precipitate this solution owing to the stability of the complex thio-germanic ion which is present; and indeed a large excess of mineral acid must be used to complete the precipitation.

Germanium disulphide is a white powder difficult to wet with water, but soluble in 221.9 parts of water, forming a solution which will precipitate various less soluble metallic sulphides. The aqueous solution quickly decomposes, with evolution of hydrogen sulphide. This sulphide readily dissolves in alkali hydroxide solution with formation of thio-germanate, a derivative of thio-germanic acid which is probably  $\text{H}_2\text{GeS}_3$ .

**Germanium Ultramarine.**—When germanium oxide, sodium carbonate, and sulphur are fused together a blue colour results. This is probably due to the formation of germanium ultramarine, an analogue of ultramarine in which  $\text{GeO}_2$  takes the place of  $\text{SiO}_2$ .<sup>1</sup>

#### \*DETECTION AND ESTIMATION OF GERMANIUM

Germanium compounds do not colour the Bunsen flame, but the spark spectrum of the element shows a number of bright lines, especially in the blue and violet.

From germanous solutions alkalis precipitate the yellow hydroxide, potassium ferrocyanide the white ferrocyanide, hydrogen sulphide the brown sulphide  $\text{GeS}$ ; germanous solutions reduce chromate and permanganate and precipitate gold from the chloride.

Alkalis yield no precipitate with germanic solutions, since hydrated germanic oxide becomes colloidal and excess of alkali forms germanate. Ammonia and ammonium and sodium carbonates partially precipitate the hydrated dioxide. The most characteristic reaction is the formation of the white sulphide, soluble in excess of ammonium sulphide; this compound serves for the gravimetric estimation of germanium.

<sup>1</sup> See this series, vol. IV.

## CHAPTER VIII

### TIN AND ITS COMPOUNDS

#### TIN (*Stannum*)

Symbol, Sn. Atomic weight, 118.7 (O = 16)

**Occurrence.** Tin rarely occurs native. It has been found in gold sand at Tipuani in Bolivia,<sup>1</sup> in small quantities in Siberia and Guiana, and in bismuthite from Mexico.

*Cassiterite* or *tinstone*,  $\text{SnO}_2$ , containing when pure 78.6 per cent. of the metal, is the only important ore of tin. It is found in lodes or veins in granite and metamorphic schistose rocks, in "Stock-works," i.e. small ramifying veins, and in pockets, as well as in beds or flats. Such tin ore is called *lode-tin*. The same ore is also found in alluvial deposits in the form of water-worn nodules, and is then known as *stream-tin*. When it possesses a fibrous structure it is called *wood-tin*.

Cassiterite is usually accompanied by quartz, mica, fluorspar, apatite, felspar and other silicates, the sulphides of various metals -- mispickel, magnetic iron ore, native bismuth, wolfram, and molybdenite. On account of the removal of foreign materials by water, stream-tin, though not so plentiful, is purer than lode-tin.

The most important European locality in which tinstone is found is still its ancient source -- Cornwall and Devon. Tinstone is also found in Saxony, Bohemia, Spain, Portugal, France, the United States, Chili, Peru, China, Japan, the Malay Peninsula, and the adjacent islands: Banca, Java, Billiton, Sumatra, and Ceylon; also in New South Wales, Queensland, Western Australia, Tasmania, and some parts of Africa. The greatest quantity of tin is obtained from Cornwall, the East Indies, Australia, and Bolivia.

Another mineral containing tin is *tin pyrites* or *bell-metal ore*, which is an isomorphous mixture of the sulphides of tin, zinc, iron, and copper. It is found at Huel Rock, St. Agnes, Cornwall, but on account of its rarity is not worked. Tin is also found in small quantity in *epidote*, *columbite*, and *tantalite*, in mineral waters, and in some meteorites.

**History.**—The use of tin as a constituent of bronze dates back to prehistoric times. The age of bronze, which in some countries intervened between the age of stone and that of iron, is considered by Montelius<sup>2</sup> to date back in the case of Britain to 2500 B.C. The "tin" of the Old Testament, which is a translation of the Hebrew word *bedhil* and appears as the Greek word *κασσίτερος* in the Septuagint, is probably a copper-tin alloy which was known in Egypt in 1600 B.C.

<sup>1</sup> Forbes, *Phil. Mag.*, 1865, [iv], 30, 139

<sup>2</sup> Montelius, *Archæologia*, 1909, 61, 97; see Cowland, "The Huxley Memorial Lecture for 1912," *J. Roy. Anthropol. Inst.*

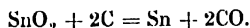


Ancient bronze (Gr. χαλκός, L. *aes*) was an alloy of copper with a little tin, and was employed by the Greeks for coinage till 400 B.C., when the tin began to be displaced by lead. About the Christian era the word *κασσιτερος*, which is probably connected with the Arabic "Kasdir," meaning tin, came to be applied to this metal; so the British Isles, whence Julius Caesar brought tin, were called the Cassiterides. Tin was also known about this time as *plumbum album* or *candidum*, in contradistinction to lead, which was *plumbum nigrum*; and Caesar has the following passage about this metal in *Bellum gallicum*, v, 12: "Nascitur ibi (in Britannia) plumbum album in medus regionibus, in maritimis ferum, sed eius exigua est copia; aere utuntur importato"; whilst Pliny<sup>1</sup> thus describes the source of the metal: "Ex adverso Celtiberiae complures sunt insulae, Cassiterides dictae graecis, a fertilitate plumbi."

The Phoenicians are said to have brought tin from the Cassiterides; and during the Roman occupation of Britain tin was taken from the Cornish mines across to Iktis or St. Michael's Mount at low water, whence it was shipped to Gaul and carried *via* Marseilles to Italy; it was also obtained about the same time from Spain and Portugal. It would appear from the names applied to tin and lead that these metals were recognised as distinct species; that they were regarded, however, rather as varieties of one metal is shown by the following passage of Pliny: "Sequitur nature plumbi ejus duo genera, nigrum atque candidum." The word stannum is found in the writings of Pliny, but it appears to have been used at that time, not for tin, but for lead and its alloys; it was first applied to tin in the fourth century of our era. Some interesting information concerning the preparation and uses of tin is contained in a Greek papyrus of the third century, discovered at Thebes and preserved in the Museum of Antiquities at Leyden.<sup>2</sup> In the Latin works of the thirteenth century which are professedly translations of the Arabian alchemist Geber (*b. v.d. 765*) some important properties of metallic tin are mentioned, such as its "ery" and its power of imparting brittleness to alloys. On account of this latter property tin was called by the Western alchemists *diabolus metallorum*. Tin was one of the original metals associated by the alchemists with Greek mythology. By the Greek alchemists it was termed Heracles; but later, about the beginning of the sixth century, it was identified with Zeus or Jupiter, and received the sign: ♃.

#### THE METALLURGY OF TIN

The essential reaction for obtaining tin from tinstone in the dry way is very simple. It consists in the reduction of the oxide with carbon thus:



Owing, however, to the large proportion of foreign matter in the ore, considerable preliminary treatment is necessary, as well as the refining of the liberated metal. Processes are also in use for extracting the metal in the wet way and by electrometallurgy.

<sup>1</sup> Pliny, *Natural History*, 4, 22.

<sup>2</sup> Reuvens and Leemans, *L'apryrus grecs du Musée d'Antiquités de Leyde*, Tomo II (E. J. Brill, 1885).

**Extraction of Tin in the Dry Way.**—This process involves the following operations:

- (i) Purification of the ore.
- (ii) Reduction of stannic oxide.
- (iii) Recovery of tin from slags.
- (iv) Refining of tin.

(i) *Purification of the Ore*—Tinstone may contain originally as little as between 1 and 2 per cent. of the metal; by the processes of purification this proportion is raised to between 50 and 70 per cent. The impurities in the ore have not simply a negative influence; they are positively injurious for two reasons. (i) The oxides of heavy metals, especially ferric oxide, would be reduced at the same time as the tin and the metals alloy with it. (ii) Silica and alkalis combine with stannic oxide to form respectively silicate of tin and alkali stannate, and in both cases tin would enter the slag. Moreover, tin ore frequently contains wolfram,  $(\text{Fe}, \text{Mn})\text{WO}_4$ , and scheelite,  $\text{CaWO}_4$ , which must be removed, as well as arsenic and sulphur in the form of arsenical and common pyrites, which may be oxidised and vapourised by roasting. The processes by which the ore is purified are threefold: (1) dressing, (2) roasting, (3) lixiviation.

(1) The dressing of the ore secures the removal of a large proportion of siliceous gangue. The ore is crushed and washed to remove the lighter particles of gangue, this being easily effected owing to the high density of the stannic oxide.

(2) The roasting process converts sulphur into sulphur dioxide, which escapes, and arsenic into arsenious oxide, which is condensed, though some of this element remains as ferric arsenate, which needs to be specially reduced. The ore, after roasting, contains besides stannic oxide, oxides of iron, copper, and bismuth, sulphates of copper and iron, tungsten compounds, and small quantities of unaltered sulphides and arsenides.

The roasting process is carried out in furnaces provided with fixed or movable roasting chambers.

A furnace with a fixed roasting chamber, such as is employed in Saxony, is shown in Fig. 9. The ore is dried on the roof of the furnace and then dropped through the opening *A* into the roasting chamber *B*. A sliding door leading to the chimney *D* can be opened or closed at will, and the same applies to the damper leading to the flue *E*. By this flue the arsenious oxide vapour passes to chambers where it is condensed.

An important form of movable roaster is Oxland and Hocking's revolving calciner, which is used in Cornwall for ores rich in sulphur and arsenic.

The calciner, shown in Fig. 10, consists of a cylinder, *B*, 30 to 40 feet long and from 4 to 6 feet in diameter; it is built of boiler-plate and lined with firebrick. The inclination of this cylinder depends upon the rate at which it is desirable to roast the ore; it makes from 3 to 8 revolutions per minute. The ore, which is dried on the roof of the condensing chamber, is fed in through the hopper *A*, and is distributed within the revolving cylinder *B* by means of four longitudinal ridges. Hot gases from the fire at *C* are drawn with air up the cylinder, and the arsenious oxide formed by the volatilisation and oxidation of the

arsenic in the ore is condensed and deposited in the series of chambers, *D*, shown at the right of the figure, while the calcined ore drops through the opening in the arch fixed at the lower end of the cylinder into the chamber *E*. From 20 to 25 tons of ore can be roasted *per diem* in this calciner, 1 cwt. of coal being required per ton of ore.

(3) The roasted ore is next lixiviated to remove soluble oxidation products. If copper sulphate is present it is washed out with water, after which hydrochloric acid is employed to extract oxides of copper, iron, and bismuth. The copper is precipitated from solution by iron, and the bismuth by water, as oxvelchloride.

Tungsten compounds are removed from the ore at this stage by means of a magnetic separator, which attracts the wolfram, or by an

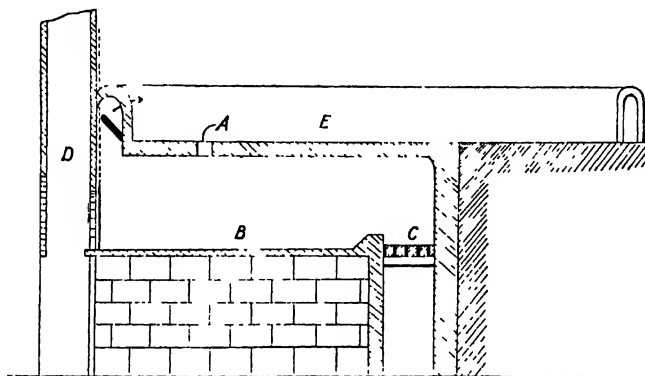


FIG. 9. Furnace for tin ores, with fixed roasting chamber (Saxony)

*A* Opening through which the ore enters the chamber after being roasted on the roof *B* Roasting chamber *C* Fireplace *D* Chimney *E* Flue by which arsenious oxide passes to condensing chambers

oxidising fusion with sodium sulphate, which converts the tungsten into sodium tungstate.

(ii) *Reduction of Stannic Oxide*.—The reduction of stannic oxide to metal, by smelting it with charcoal or anthracite, is carried out either in shaft furnaces, constructed on the principle of the blast-furnace used in iron-smelting, or in reverberatory furnaces. The former method is adopted in Saxony, Bohemia, Finland, Bolivia, Burma, Siam and the Malay Peninsula, Banca, Biliton, South China, and Japan; the latter in England, France, Germany, Spain, Mexico, California, and the Malay Peninsula.

A shaft furnace, as used in Saxony, is about 10 ft. high, is built of granite or gneiss, and is lined with granite. It is trapezoidal in cross-section and tapers towards the base. The blast is conveyed by two tuyères which enter the furnace at the back. The molten products pass through the "eye" at the base of the furnace into the forehearth, where the slag and tin separate from each other. The metal obtained in this process contains about 97 per cent. of tin, the rest being copper and iron; the slag consists chiefly of silica, ferrous

## TIN AND ITS COMPOUNDS

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oxide, and stannic oxide and may contain as much as 30 per cent. of the latter substance.

A reverberatory furnace, such as is used in Cornwall consists of a

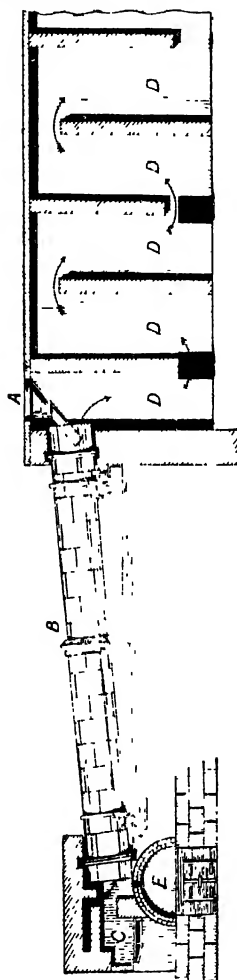


Fig. 10.—Oxide and Hopper. The charge is introduced by the hopper A, and the oxide is removed by the door D. The charge is introduced by the hopper A, and the oxide is removed by the door D.

shallow elliptical bed, which may be 14 to 18 ft. long and 8 to 12 ft. wide (A, Fig. 11). The bed is made of firebrick and lasts about three months; it slopes towards the middle and to the taphole. The charge is introduced by a door C opposite the taphole and worked through another door D opposite the firebridge. The whole process lasts from

six to twelve hours, and the impure tin is run off into a kettle or float placed to receive it. The slag produced is variable in composition. Some is so poor in tin that it may be thrown away; other contains "prills" of metal, or is rich enough in stannic oxide to merit further treatment.

(iii) *Recovery of Tin from Slags*.—The tin contained in slags is either in the form of mechanically enclosed metal, or as stannic oxide combined with silica. The free metal may be recovered by crushing the slag and washing it, or by the settling out of the metal in the molten condition. The metal is obtained from the combined oxide either by *reduction* or *precipitation*. Reduction consists in resmelting with coal after the addition of a stronger base, such as lime, which liberates the stannic oxide from the silica; precipitation is smelting with iron, which displaces tin, forming ferrous silicate.

(iv) *Refining of Tin*.—Crude or raw tin from the shaft or reverberatory furnace contains small quantities of iron, lead, antimony, and arsenic, which are removed by the process of refining. This consists of *liquation* and *boiling* and *tossing*.

*Liquation* is the gradual heating of the metal till the pure and more fusible tin melts and runs away, leaving behind the less fusible *liquation-dross*. It is carried out in Saxony and Bohemia directly the metal has been tapped from the forehearth of the shaft furnace, upon the liquation-hearth, which is simply an inclined plate with ridges upon it, down which the purified molten metal runs. In the English process the tin is remelted and liquated in either the same or a specially constructed reverberatory furnace, and then boiled in the refining pot or kettle. This *boiling* consists in stirring with a bundle of green twigs the molten metal kept hot by a fire underneath the pot. The dry distillation of the wood generates gas which keeps up a bubbling action within the molten metal and secures its exposure to the air. The dross or *boil-scum* is removed from the surface of the metal. *Tossing* consists in removing the liquid metal from the pot in a ladle and pouring it back again from a height. This likewise secures aeration and oxidation of impurities, which are similarly removed.

For the **extraction of tin in the wet way** various chemical methods have been devised, but they have been applied chiefly to the *recovery of tin from tin-plate*, and result in the preparation of tin salts rather than the metal itself. Obsolete methods<sup>1</sup> consisted in dissolving the tin from the plate in acid or alkali and then precipitating the metal from solution with iron or zinc, or preparing the oxide and smelting it with coal. Among the methods now in use is that of attacking the plate with chlorine gas and obtaining a solid hydrate of stannic chloride.<sup>2</sup> An electrolytic method consists in packing loosened chips of tin-plate in wire baskets immersed in hot caustic soda solution. These baskets serve as anodes, whilst the iron vessel containing the soda is made the cathode. The tin is obtained as a spongy mass on passing a current of 1.5 volt.

**Electrometallurgical Processes** have been applied to the extraction of tin from its ores and slags, but without much success; the metal is recovered from tin-plate, however, and is also refined successfully

<sup>1</sup> For a detailed account of these methods see *Handbook of Metallurgy*, by Schnabel and Lewis (Macmillan & Co.), 2nd edn., 1907, vol. II, p. 540.

<sup>2</sup> *Ibid.*, see also article in *American Machinist*, 1914, 40, 791.

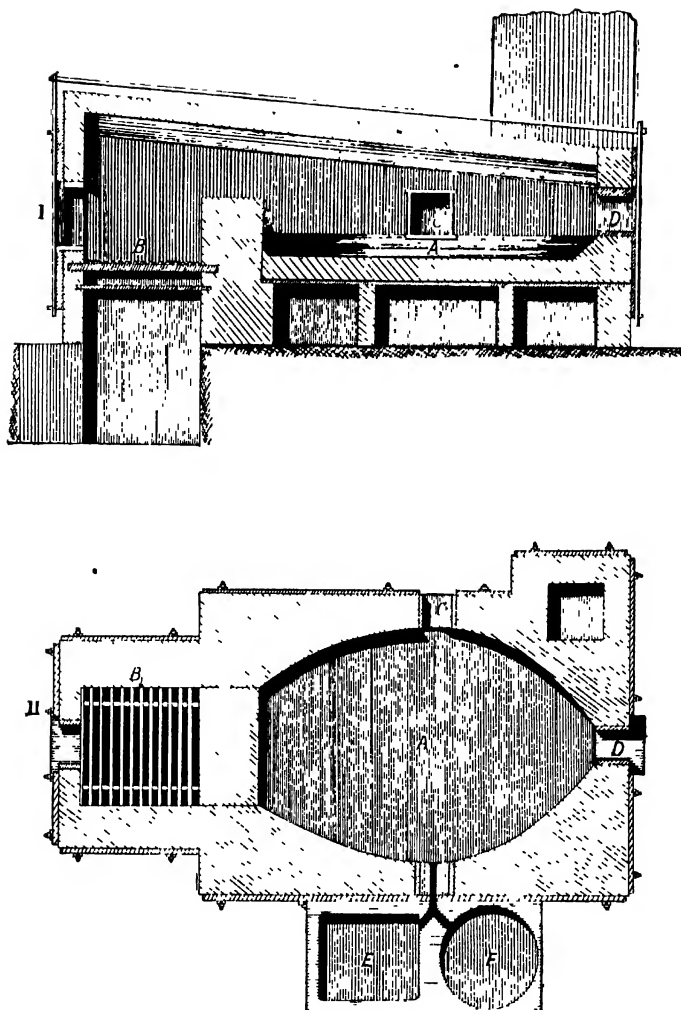


FIG. 11. — Reverberatory furnace for tin smelting. I. Elevation. II. Plan.

A. Hearth or bed of furnace. B. Fireplace. C. Door for introducing charge.  
 D. Door for working charge. E. Kettle for receiving tin. F. Kettle for  
 receiving refined tin after liquation.

by this means. Both acid and basic electrolytes, *i.e.* solutions of tin salts and of stannates or thiostannates respectively, have been used, but the latter solutions yield the better results. A solution proposed by Borchers<sup>1</sup> contains 3 to 5 per cent. of sodium stannate and 12 to 15 per cent. of common salt. The addition of the salt confers high conductivity on the solution, and enables the tin to be obtained as a spongy metallic deposit when a current of 50 to 150 amperes at 2 to 3 volts is employed, with the solution at a temperature of 40° C. to 50° C. Tin has been refined electrolytically through the medium of a solution of sodium thiostannate.<sup>2</sup>

*Commercial tin* reaches a high state of purity; it seldom contains less than 99 per cent. of the metal. Although all tin has been refined, the best quality is known as *refined tin*. It is made from the purest ores and submitted to a lengthened process of refining. The ordinary quality of tin is cast into moulds and known as *block tin*. The purity of tin may be judged by melting it and casting it in an ingot mould. The ingot should be smooth, bright, and rounded; small impurities will shapen its edges and cause it to "frost" over on solidifying whilst much impurity will give the metal a yellow or purple tinge.

*Grain tin* is produced from refined tin by heating it to a temperature a little below its melting-point to induce crystallisation and make it brittle. It is then broken by a hammer or dropped from a height. The masses thus obtained show a columnar structure.

The London Metal Exchange recognises two classes of tin. Class A containing not less than 99.75 per cent. and Class B not less than 99 per cent. of the metal; and these official brands include the following: Straits, Australian, Banca, Billiton, English, German, and Chinese.

The following analyses show the composition of typical brands of tin:

	Tin	Sb	As	Pb	Bi	Cu	Fe	Ag	S
Banca . . . . .	99.950	0.007	nil	trace	nil	0.018	0.045	nil	trace
Billiton . . . . .	99.960	0.006	nil	nil	nil	0.023	nil	nil	nil
Williams ) No 3	99.200	0.300	0.037	0.396	0.007	0.100	0.013	0.014	0.006
Harvey & Co ) No 1	99.911	0.011	0.022	trace	0.001	0.020	trace	trace	0.005
Reduth . . . . .	99.160	0.178	0.053	0.177	0.017	0.415	0.014	0.006	0.008
Chinese, No 1 . . .	99.343	0.031	0.010	0.134	0.007	0.052	0.010	trace	0.011

**Physical Properties.**—Tin exists in three allotropic modifications. The form stable at ordinary atmospheric temperature (above 18° C.) is in tetragonal crystals, which at low temperatures pass more or less rapidly into "grey tin," and at temperatures somewhat below the melting-point undergo transition into rhombic crystals. The following properties are those of **tetragonal tin**:

Tin is a white, highly lustrous metal, having a density at 16° C. of 7.301 or 7.3137 after heating to near its melting-point.<sup>3</sup> The density of the freshly fused metal is 7.287 at 15° C.<sup>4</sup> Tin expands in melting; the density of the solid metal at 226.5° C. is 7.1835, and that of the

<sup>1</sup> Borchers, *Elektrometallurgie*, p. 154.

<sup>2</sup> Claus, *Zeitsch. Elektrochem.*, 1908, 8, 168, 169.

<sup>3</sup> Sprung, *J. Chim. phys.*, 1903, 1, 593.

<sup>4</sup> Cohen and Goldschmidt, *Zeitsch. physikal. Chem.*, 1904, 50, 225.

liquid metal at the same temperature 6.988 (Cohen). The crystalline structure of the metal is well seen when tinplate is etched with hydrochloric acid containing free chlorine or with stannic chloride, a pattern (*moué métallique*) resembling frost picture, being produced. Crystallised tin is, however, best seen in the tin-tree or *arbor Jovis*, which is formed when a rod of zinc is suspended in a solution of stannous chloride (Hermann, 1786). Fine crystals of the metal are likewise obtained when water with zinc-dust in suspension is added to stannous chloride, as well as when this solution is electrolysed. The "cry" of tin, a creaking noise produced when a bar of the metal is bent, is due to the grinding of the crystals against one another. According to Gaubert<sup>1</sup> macles, *i.e.* twinned crystals, of tin may be produced on the under surface of a smooth sheet of the metal when it is suddenly pierced by a needle, and the "cry" of tin is probably due to the formation of these macles. The folding or twisting of a sheet of tin also gives rise to twinned bands. Tin is harder than lead, but softer than gold; it is malleable at ordinary temperature and can be beaten or rolled into sheet or foil; it is also ductile, increasing in ductility up to 100° C., but is not tenacious, a wire 0.08 m. in diameter breaking under a load of 51 lb.

At 200° C. tin becomes brittle and can be powdered. The mean coefficient of linear expansion of the metal between 0° C. and 100° C. is 0.00002296<sup>2</sup>; its specific heat is 0.0521 at 18° C. and 0.0561 at 100° C.,<sup>3</sup> whence the atomic heat is 6.2 and 6.7 respectively. The thermal conductivity at 18° C. of block tin is 0.1453 gram calories, and of tin-wire 0.1519 gram calories; whilst the electric conductivities of these two forms of the metal at 18° C. are  $8.28 \times 10^4$  and  $8.82 \times 10^4$  units respectively.<sup>4</sup> Tin obeys the law of Wiedemann and Franz that  $\frac{\lambda}{K} =$  constant, where  $\lambda$  is thermal and K electric conductivity and also the law of Lorenz that this ratio is proportional to the absolute temperature.<sup>5</sup>

As with many other metals, the melting-point of tin has been variously given. The most reliable results are those of Wadner and Burgess,<sup>4</sup> who give the value 231.9° C.<sup>5</sup> Other rather but less reliable results are those of Heycock and Neville<sup>6</sup> and Bogaderow.<sup>7</sup> The former observers found the melting-point to be 231.5° C., the latter 231.14° C. and 231.25° C., whilst for the purest English tin, containing only a trace of iron, arsenic and phosphorus, Bogaderow found 230.92° C. Tin is said to volatilise between 1450° C. and 1600° C. (Carnelley and Williams), but its boiling-point, which is very high, is not known with accuracy. Greenwood<sup>8</sup> gives the value 2270° C. Various alloys of tin have been fractionally distilled in the electric furnace.<sup>9</sup> The

<sup>1</sup> Gaubert, *Compt. rend.*, 1914, 159, 680, cf. Ewing and Rosenham, *Phil. Trans.*, 1900, A, 193, 353, 1901, A, 195, 271.

<sup>2</sup> Matthiessen, *Proc. Roy. Soc.*, 1866, 15, 220.

<sup>3</sup> Jaeger and Dieckhoist, *Wissenschaftl. Abhandl. phys. tech. Reichsanst.*, 1900, 3, 269.

<sup>4</sup> Wadner and Burgess, *Pyron Standard*, Washington, 1910, 6, 149, 1910, 7, No. 1.

<sup>5</sup> On the constant volume nitrogen thermometer scale.

<sup>6</sup> Heycock and Neville, *Trans. Chem. Soc.*, 1890, 57, 376.

<sup>7</sup> Bogaderow, *Zeitsch. anorg. Chem.*, 1893, 4, 474.

<sup>8</sup> Greenwood, *Proc. Roy. Soc.*, 1909, A, 82, 396, 1910, A, 83, 183.

<sup>9</sup> Moissan and O'Farrelley, *Compt. rend.*, 1904, 138, 1651.



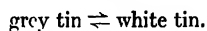
spectrum of tin has been studied by Lohuizen, who has expressed the relationships between its lines by means of a formula.<sup>1</sup>

The most intense lines in the spectrum of tin are as follow<sup>2</sup>:

Arc: 2840.17, 2863.53, 3009.33, 3031.25, 3175.16, 3262.50, 3330.80,  
3801.19, 4521.90

Spark: 2840.10, 2863.33, 3175.15, 3262.48, 3801.32, 4521.90, 4585.80,  
6153.00

**Grey Tin.**—In 1851 O. L. Erdmann discovered organ-pipes covered with warty excrescences which developed into holes owing to the conversion of the tin into a grey powder. Similar observations have been repeatedly made. Aristotle speaks of tin "melting" at low temperature; and bars of tin kept at Petrograd and Moscow during severe winters have been found covered with a grey powder owing to what has been called "tin-pest"; whilst coins and utensils made of tin, preserved in museums, have developed spots upon their surfaces owing to the contraction of "museum-sickness"! The cause of this behaviour of tin has been investigated by Cohen and van Eijk,<sup>3</sup> who have shown that tin is enantiotropic-- that is, it exists in two allotropic modifications which change the one into the other with change of temperature according to the scheme:



The transition temperature<sup>4</sup> at which both forms are equally stable lies very near 20° C.; above this temperature ordinary white tin is stable, below it metastable. Consequently when the metal is kept below 20° C. it continuously changes into the grey form. Under ordinary atmospheric conditions the rate of this change is very slow, but it is accelerated by lowering of temperature, reaches its maximum at about -50° C., and then diminishes again. Fig. 12 sets forth the experimental results of Cohen and van Eijk.<sup>5</sup> The density of grey tin is not known accurately, but it is about 5.8 at 15° C.

**Rhombic Tin.**—Another modification of tin, occurring in rhombic crystals,<sup>6</sup> is formed when tin cools slowly from the molten state; and it is probable that gram tin owes its peculiar structure to this modification. Rhombic tin is also metastable at atmospheric temperature, the transition temperature between this form and tetragonal tin being variously given as 161° C.,<sup>7</sup> 170° C.,<sup>8</sup> and 202.8° C.<sup>9</sup> The heat of transformation of tetragonal into rhombic tin is 14.03 ± 0.002 calories per gram, and the volume change 0.00017 c.c. per gram.<sup>10</sup> The density of rhombic

<sup>1</sup> Lohuizen, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 31.

<sup>2</sup> Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

<sup>3</sup> Cohen and van Eijk, *Zeitsch. physikal. Chem.*, 1899, 30, 601, 1908, 63, 625, 1909, 68, 214.

<sup>4</sup> See also Jancke, *Zeitsch. physikal. Chem.*, 1915, 90, 313.

<sup>5</sup> Cohen and van Eijk, *Zeitsch. physikal. Chem.*, 1899, 30, 617.

<sup>6</sup> Trechmann, *J. Miner. Soc.*, 1880, 3, 186, von Foullon, *Jahrb. k. k. geol. Reichsanst.*, 1884, 367, Cohen and Goldschmidt, *Zeitsch. physikal. Chem.*, 1901, 50, 225.

<sup>7</sup> Degens, *Dissertation*, Delft, 1908.

<sup>8</sup> Cohen and Goldschmidt, *loc. cit.*

<sup>9</sup> Smits and de Leens, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 676; see also *Ann. Phys.*, 1903, [iv], 10, 147.

<sup>10</sup> Werner, *Zeitsch. anorg. Chem.*, 1913, 83, 275.

tin—slightly impure—is 6.525 to 6.557 at 15.8° C. (Trechmann). The relations between the three varieties of tin may thus be set forth:

- (1) Grey tin  $\rightleftharpoons$  tetragonal tin, 20° C.
- (2) Tetragonal tin  $\rightleftharpoons$  rhombic tin, 161° C. to 202.8° C.
- (3) Rhombic tin  $\rightleftharpoons$  molten tin, 231.9° C.

The heat of transformation of white into grey tin at 273 abs is 532 calories per gram-atom.<sup>1</sup>

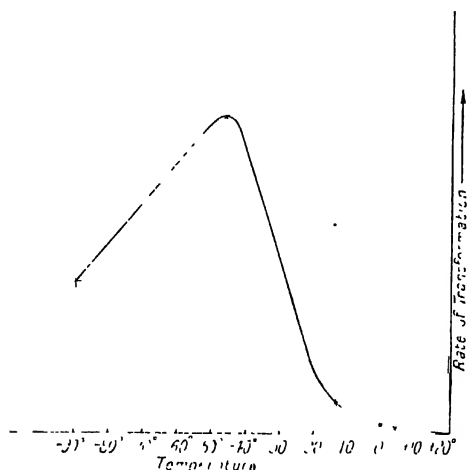
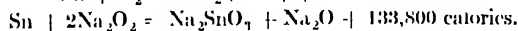
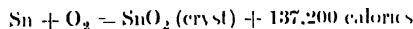


Fig. 13.—The transformation of white into grey tin.<sup>2</sup>

**Chemical Properties.** Metallic tin remains bright in moist air at ordinary temperatures, but is oxidised when sufficiently heated in the air. Thus molten tin becomes covered with a grey film containing stannous oxide, which is gradually oxidised to cream-coloured stannic oxide. Tin also burns to dioxide when sufficiently heated in the air, and likewise decomposes steam at a red heat with formation of the same oxide. The following thermal values have been established by Mixer<sup>3</sup>:



In the electropotential series of the metals tin stands just before hydrogen; consequently tin possesses little power of displacing hydrogen from dilute acids. Cold dilute hydrochloric and sulphuric acids have very little action on tin, but concentrated hydrochloric acid dissolves the metal with a fairly brisk evolution of hydrogen and formation of stannous chloride in solution. The rate of evolution of hydrogen is increased by contact of the tin with copper, silver, or platinum, owing

<sup>1</sup> Bronsted, *Zeitsch. physikal. Chem.*, 1914, 88, 479.

<sup>2</sup> Cohen and van Eijk, *Zeitsch. physikal. Chem.*, 1899, 30, 617.

<sup>3</sup> Mixer, *Amer. J. Sci.*, 1909, [iv], 27, 229.

to electric action. Hot concentrated sulphuric acid dissolves tin with evolution of sulphur dioxide and formation of stannic sulphate, the stannous sulphate first formed being oxidised at the expense of the sulphuric acid.<sup>1</sup> Very dilute nitric acid gradually dissolves tin without evolution of gas, with the formation of stannous and ammonium nitrates; acid of density about 1.3 converts tin to a white powder, with evolution of oxides of nitrogen. This powder is hydrated metastannic acid (*q.v.*), probably formed by the decomposition of unstable stannic nitrate. Tin resembles antimony in its behaviour towards nitric acid, and this behaviour signifies the position which these metals occupy amongst the elements; that is, it shows them to be metalloids, intermediate between non-metals and metals. For representatives of these three classes of elements behave thus towards nitric acid:

Metal.	Metalloid	Non-metal.
Soluble nitrate.	Insoluble hydrated oxide.	Soluble oxyacid.

Absolute nitric acid has no action on tin. Aqua regia dissolves tin, forming stannic chloride, provided too much nitric acid is not present; otherwise metastannic acid separates. Diluted organic acids act very slowly on tin in the presence of air. The metal dissolves in warm concentrated alkalis with formation of alkali stannate and evolution of hydrogen. Stannate is formed rather than stannite owing to the superior acidity of stannic tin; indeed a solution of stannite decomposes on concentration into stannate and metallic tin.

**Uses of Tin.**—Because it resists the action of air, water and vegetable acids, and so keeps a bright surface, tin is a very useful metal for household and technical purposes. It is employed alone in place of lead for making pipes used for condensation in distilling industries, and also in the form of tin-foil, now so widely used for wrapping purposes. Its chief use, however, is as a coating for other metals, *i.e.* for tin-plate; it is also a constituent of a number of important alloys shortly to be described.

The manufacture of *tin-foil* depends on the property of tin, which it shares with other metals, of becoming malleable at an elevated temperature. Thus at 100 C. tin is sufficiently malleable to be rolled into thin sheet and foil. Tin-foil was formerly much used in an amalgamated state for making mirrors, but it has now been largely replaced by silver.

The art of tinning brass and copper was known to the Romans, and so thin was the coating obtained by them that Pliny states that copper when tinned does not increase in weight. The tinning of iron, which is the most important part of the modern industry, probably originated in Bohemia early in the seventeenth century. An English tin-plate company was formed in 1670; and the industry flourishes now chiefly in South Wales.

Formerly wrought-iron formed the basis of tin-plate, but now Siemens' mild steel is chiefly employed. Bars of mild steel are rolled into plates of suitable thickness, which are "pickled" in dilute sulphuric or hydrochloric acid, annealed, cold-rolled, reannealed at lower temperature, pickled again in weaker acid, washed with water, and introduced, wet, into the tinning machine. This consists of a box containing molten tin and divided by a partition extending into the metal. On one half of the molten metal a flux of zinc chloride floats, on the

<sup>1</sup> J. and H. S. Pattinson, *J. Soc. Chem. Ind.*, 1898, 17, 214.

other half is a layer of hot grease. The plate is passed through the flux into the molten metal and under the partition, so as to emerge through the grease. It is then passed through rollers which remove surplus tin and induce a smooth and bright surface on the plate.

Formerly the plate was treated in a series of pots, in which it was first dried in hot grease, then coated with tin, and afterwards brushed with oil to cause an alloy of tin and iron to be formed; then it was immersed in a pot of purest tin, covered with oil, to give it a second coating, and passed through rollers immersed in hot oil; it was next cooled in oil, and finally cleansed by being scrubbed with bran and chalk. Copper, brass, or iron wire is tinned by being wound off a drum through cleaning and rinsing vats and a drying medium, and then through molten tin. A vessel is tinned on its interior by means of molten tin poured into it whilst it is hot; the tin is then rubbed over the surface by rags, a little rosin or sal ammoniac being employed to prevent oxidation.

#### ATOMIC WEIGHT OF TIN

That the atomic weight of tin is approximately 119 is indicated by the following considerations.

(i) The specific heat of the cast metal between 0° C. and 100° C. is 0.0559. Assuming, in accordance with Dulong and Petit's law,<sup>1</sup> a mean atomic heat of 6.4, the atomic weight of tin must be about 115.

(ii) Stannic oxide is isomorphous with titanic oxide, whilst fluo-stannates are isomorphous with fluotitanates, etc. Analysis of these compounds and the application of Mitscherlich's law indicate an atomic weight of 119 for tin.<sup>2</sup>

(iii) There is a space in the Periodic Table for an element of atomic weight lying between 114.8 and 120.2, and the properties of tin indicate that it would fill that space very satisfactorily.

Numerous attempts have been made to determine with accuracy the atomic weight of tin, but it was not until the beginning of the year 1915 that a thoroughly satisfactory result was arrived at. The results obtained by Gay-Lussac,<sup>3</sup> Berzelius,<sup>4</sup> Mulder,<sup>5</sup> Vlaanderen,<sup>6</sup> Dumas,<sup>7</sup> and van der Plaats<sup>8</sup> are now merely of historical interest, and are briefly summarised in the table on p. 336. The value for the atomic weight of tin that was accepted by the International Atomic Weights Committee from 1903 to 1915, namely 119.0, was based solely on the work of Bongartz and Classen<sup>9</sup>; but it has now been replaced by Buseck's value, namely 118.7.

Bongartz and Classen carried out five series of experiments involving (a) the oxidation of electrolytic tin to stannic oxide; (b) electrolysis of ammonium stannichloride; (c) electrolysis of potassium stannichloride; (d) electrolysis of stannic bromide; and (e) the preparation of stannic sulphide from electrolytic tin and the estimation of its sulphur by oxida-

<sup>1</sup> See this series, vol. 1, p. 89.

<sup>2</sup> See remarks on Titanium, p. 235.

<sup>3</sup> Gay-Lussac, *Ann. Chim.*, 1811, 80, 163.

<sup>4</sup> Berzelius, *Göteborgs Annalen*, 1812, 40, 272.

<sup>5</sup> Mulder, *J. prakt. Chem.*, 1849, 48, 35.

<sup>6</sup> Vlaanderen, *Jahresber.*, 1858, p. 183.

<sup>7</sup> Dumas, *Ann. Chim. Phys.*, 1859, [iii], 55, 156.

<sup>8</sup> Van der Plaats, *Compt. rend.*, 1885, 100, 52.

<sup>9</sup> Bongartz and Classen, *Ber.*, 1888, 21, 2300.

dissolving to sulphate and precipitating as barium sulphate. The mean result deducible from the ratios found by these investigators is Sn = 119.05.

Six years later Schmidt<sup>1</sup> made a single determination of the atomic weight of tin, which yielded the value 118.49. Meyer and Kerstein<sup>2</sup> as the result of two determinations of the ratio Sn : SnO<sub>2</sub> found the value 117.54.

Undoubtedly the most accurate work is that recently published by Briscoe,<sup>3</sup> who determined the value for the ratio SnCl<sub>4</sub> : 4Ag. Stannic chloride was prepared by direct union of its elements, purified by fractional distillation, and collected and sealed in glass bulbs. The chlorine was estimated by breaking one of the bulbs in a solution of silver in nitric acid, whereby silver chloride was precipitated—the process being completed by subsequent addition of silver nitrate solution, and finally by titration with standard silver nitrate or sodium chloride solution, according to circumstances. The process of the titration and the attainment of the end-point were ascertained nephelometrically. From the mean of fifteen highly concordant experiments the atomic weight of tin was found to be 118.698.

The following table summarises the results of the different investigators referred to above:

Authority	Ratio Measured	No. of Experiments	Atomic Weight of Tin <sup>4</sup>
Gay Lussac, 1811	Sn : SnO <sub>2</sub> = 100 : 127.2	1	117.6
Berzelius, 1812	Sn : SnO <sub>2</sub> = 100 : 127.2	1	117.6
Mulder, 1819	Sn : SnO <sub>2</sub> = 100 : 127.517	3	116.3
Vlaanderen, 1858	Sn : SnO <sub>2</sub> = 100 : 127.082	2	118.2
Dumas, 1859	Sn : SnO <sub>2</sub> = 100 : 127.105	2	118.06
	SnCl <sub>4</sub> : 4Ag = 60.207 : 100	2	117.98
Van der Plaats, 1885	Sn : SnO <sub>2</sub> = 100 : 127.102	7	118.07
Bongartz and Classen, 1888	Sn : SnO <sub>2</sub> = 100 : 126.877	11	119.06
	Sn : (NH <sub>4</sub> ) <sub>2</sub> SnCl <sub>6</sub> = 32.369 : 100	16	119.09
	Sn : K <sub>2</sub> SnCl <sub>6</sub> = 29.010 : 100	10	119.07
	SnBr <sub>4</sub> : Sn = 100 : 27.123	10	118.97
	Sn : 2BaSO <sub>4</sub> = 100 : 392.056	8	119.08
Schmidt, 1894	Sn : SnO <sub>2</sub> = 0.5243 : 0.6659	1	118.49
Meyer and Kerstein, 1913	Sn : SnO <sub>2</sub> = 1.9719 : 2.5087	2	117.54
Briscoe, 1915	SnCl <sub>4</sub> : 4Ag = 60.3742 : 100	15	118.698

<sup>1</sup> F. W. Schmidt, *Ber.*, 1894, 27, 2743

<sup>2</sup> Meyer and Kerstein, *Ber.*, 1913, 46, 2882

<sup>3</sup> Briscoe, *Trans. Chem. Soc.*, 1915, 107, 63

<sup>4</sup> In calculating the atomic weights from the ratios given in this table the following fundamental values have been used: O = 16.000, H = 1.00762, Cl = 35.457; Br = 79.916, Ag = 107.880, Ba = 137.363, N = 14.008, K = 39.100, S = 32.065.

The figure **118.70**, which appears to approach very closely to the true value, was in 1916 accepted by the Atomic Weights Committee.

## ALLOYS OF TIN

Tin forms many important alloys, and these may be divided into two classes: those which contain copper and those which do not.

**Tin-Copper Alloys.** The properties of the copper-tin alloys, the bronzes, bear no definite relation to those of their constituent metals. Whilst tin itself is soft and fusible, its progressive addition to copper produces the following changes. Five per cent. of tin yields a nearly copper-coloured alloy which is tough and strong and much harder than copper, so that it may be employed for coinage and for engraving work. Ten per cent. of tin gives a rich yellow alloy which is still harder, so that it must be cast, and with the addition of more tin up to 20 per cent. the alloy becomes sonorous, though somewhat brittle, but suitable for making small bells. With further addition of tin up to 24 per cent. an alloy is obtained out of which the largest bells are cast; it is decidedly brittle and has a grey fracture. When 33 per cent. of tin is reached the alloy is white and constitutes speculum metal, and is so brittle that it may be powdered in a mortar. The brittleness continues till about 65 per cent. of tin is present, after which the hardness diminishes as pure tin is approached.

The tin-copper alloys are here summarised<sup>1</sup>:

<i>Percentage of Tin</i>	<i>Nature of Alloy</i>
5	Bronze for coinage and medals (a little tin often replaced by zinc), Roman nails, engineers' soft gun-metal or "brasses."
7	Bronze suitable for mathematical instruments.
8.5	Bronze suitable for wheels to be cut with teeth.
8-12	Soft bronze of the ancients; 9-10 per cent. for gun-metal; 10-12 per cent. for medium engineers' "brasses."
12-14.5	Hard bronze of the ancients, used for weapons and tools. Now used for engineers' hard bearings.
16	Soft musical bells.
18-20	Chinese gongs and cymbals.
20	Small house bells; Indian gongs.
22	Large house bells.
24	Limit for large church bells.
33	Often also a little arsenic. Speculum metal.
66	"Temper," an alloy used to harden pewter.

Bronze is hardened by a process opposite to that employed with steel. Instead of being suddenly cooled by plunging into water, it is slowly cooled to induce hardness; if suddenly cooled it becomes soft and malleable. This difference is due to the different kinds of

<sup>1</sup> Vide Thorpe, *Dictionary* vol. v, art. Tin (1913).

crystals that are formed at different temperatures.<sup>1</sup> Repeated hammering and cold working of bronze greatly increases its hardness.

Two compounds of copper and tin are known<sup>2</sup>:  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_2\text{Sn}$ . The existence of these compounds, however, is probably insufficient to account for the remarkable differences in properties between the various alloys and their constituent metals. These alloys are probably to be regarded as mixtures of one or two definite compounds with excess of a solid solution of tin in copper. The electrical properties of copper-tin alloys have been studied by Ledoux.<sup>3</sup>

*Bronze bearing metal*, employed for the bearings of locomotives, is an alloy composed of copper 77, tin 8, lead 15 parts. The presence of lead diminishes loss by wear and reduces local heating. The function of the tin is to provide a solvent medium for copper and lead, which do not mix well.

*Phosphor-bronze* is bronze containing 5 to 15 per cent. of tin and from a trace to 1.75 per cent. of phosphorus, added in the form of phosphor-tin. The phosphorus confers greater hardness, elasticity, and toughness upon the alloy. Manganese and silicon bronzes are also in vogue, but they contain little, if any, tin.

**Other Tin Alloys.** Tin enters into the composition of the following alloys, which contain little or no copper: common pewter, soft solder, type-metal, Britannia metal, plate-pewter, white bearing metal, and the various fusible metals. Only soft solder and common pewter will be considered here; the other alloys contain antimony or bismuth and will be discussed in Volume VI of this series.

Tin and lead will mix in all proportions; the alloys produced are more fusible than either separate metal, and are likewise harder and tougher. There is no evidence, however, of the existence of any compound of the two metals. The lead-tin eutectic point lies at  $181^\circ\text{C}$ . at 24.4 atomic per cent.  $\text{Pb}^4$  ( $\approx 36.0$  per cent.  $\text{Pb}$  by weight).

No	Tin	Lead	Melting-point $^\circ\text{C}$	No	Tin	Lead	Melting-point $^\circ\text{C}$
	Pure	lead	327 <sup>1</sup>	7	11 $\frac{1}{2}$	1	168 <sup>6</sup>
1	1	25	292 <sup>2</sup>	8	2	1	171 <sup>1</sup>
2	1	10	283 <sup>2</sup>	9	3	1	180 <sup>1</sup>
3	1	5	266 <sup>3</sup>	10	4	1	185 <sup>2</sup>
4	1	3	250 <sup>1</sup>	11	5	1	192 <sup>1</sup>
5	1	2	227 <sup>1</sup>	12	6	1	194 <sup>1</sup>
6	1	1	188 <sup>1</sup>		Pure	tin	231 <sup>1</sup>

*Soft solders* are alloys of tin and lead in varying proportions; they occasionally contain bismuth, which lowers their melting-point. The

<sup>1</sup> Vide Desch, *Metallography* (Longmans), 1910, p. 319.

<sup>2</sup> Desch, *J. Inst. Metals*, 1909, 1, 227.

<sup>3</sup> Ledoux, *Compt. rend.*, 1912, 155, 35.

<sup>4</sup> Degens, *Zeitsch. anorg. Chem.*, 1909, 63, 207, see also Guertler, *Zeitsch. Elektrochem.*, 1909, 15, 123, 933; Mazzotto, *Nuovo. Cim.*, 1910, [v], 19, 1 215; and *Int. Zeitsch. Metallographie*, 1911, 1, 289.

table on the previous page (Tomlinson), showing the composition of soft solders, with their melting-points, illustrates the influence of admixture upon the melting-points of metals.

Ordinary soft plumbers' and tinmen's solder is made of equal parts of tin and lead; fine tinmen's solder contains 2 parts of tin to 1 of lead.

*Common Pewter.*—The toughest and hardest variety of pewter contains 3 parts of tin to 1 of lead, the proportion may, however, rise as high as 1 of tin to 1 of lead.

The following bibliography of the alloys of tin may prove useful:

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Antimony and manganese	Williams, <i>Zeitsch anorg Chem</i> , 1907, 55, 1
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Bismuth	Lewis, <i>Phil Mag</i> , 1904, 17, 8, 19 Mama, <i>J Russ Phys Chem Soc</i> , 1908, 40, 393
Bismuth and lead	Shepherd, <i>J Physiol Chem</i> , 1902, 6, 319
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Cadmium and zinc	Lorenz, <i>Zeit chem anorg Chem</i> , 1911, 83, 445 Vashin, <i>J Russ Phys Chem Soc</i> , 1914, 46, 223
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Iron	Isaac and Tammann, <i>Zeitsch. anorg. Chem.</i> , 1907, 53, 281
Lead	Saunders, <i>Chem. Zentr.</i> , 1904, 1, 863, n, 1022 Gusta, <i>ibid.</i> , 1906, 1, 1462 Brag, <i>Bull. Soc. chim.</i> , 1907, [iv], 1, 905 Resingham and Tucker, <i>Phil. Trans.</i> , 1908, A, 209, 89 Sapozhnikov, <i>J. Russ. Phys. Chem. Soc.</i> , 1908, 40, 92 Holzmum, <i>Pharm. Zentr. h.</i> , 1908, 49, 117 Degens, <i>Zeitsch. anorg. Chem.</i> , 1909, 63, 207 Guertel, <i>Zeitsch. Elektrochem.</i> , 1909, 15, 12, 953 Mazzotto, <i>Nuovo Cim.</i> , 1910, [v], 19, 1, 215 Lut. <i>Zeitsch. Metallographie</i> , 1911, 1, 289
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Silver	Petrenko, <i>ibid.</i> , 1907, 53, 200
Sodium	Moissan and Watanabe, <i>Compt rend</i> , 1907, 144, 16 Mathewson, <i>Zeitsch. anorg. Chem.</i> , 1905, 46, 94
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## COMPOUNDS OF TIN

Tin forms two series of compounds in which the metal is bi- and quadri-valent respectively. No hydride is known to exist, but various stannic alkyls have been obtained, as well as other compounds containing hydrocarbon radicals, which elucidate the analogy between tin and carbon. Stannous oxide is sufficiently basic to form a sulphate and an unstable nitrate; stannic oxide forms a sulphate, but scarcely a nitrate, and it is characterised by the power to polymerise, forming  $\beta$ -mactannic acid and its derivatives.

The following are the chief compounds of tin:

	BIVALENT TIN	QUADRIVALENT TIN
Organo-metallic compounds		$\text{Sn}(\text{CH}_3)_4, \text{Sn}(\text{C}_2\text{H}_5)_4$ , etc.
Fluorides	$\text{SnF}_2, \text{HSnF}_3, \text{H}_2\text{SnF}_4$	$\text{SnF}_4, \text{K}_2\text{SnF}_6$
Chlorides	$\text{SnCl}_2, \text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , and other hydrates	$\text{SnCl}_4$ , various hydrates, $\text{K}_2\text{SnCl}_6$
Bromides	Salts of $\text{HSnCl}_3$ and $\text{H}_2\text{SnCl}_4$ , $\text{SnBr}_2$ , salts of $\text{HSnBr}_3$ and $\text{H}_2\text{SnBr}_4$	$\text{SnBr}_4, \text{H}_2\text{SnBr}_6$
Iodides	$\text{SnI}_4, \text{SnI}_2 \cdot 2\text{H}_2\text{O}, \text{KSnI}_4$	$\text{SnI}_4$
Oxides	$\text{SnO}$	$\text{SnO}_2$
Hydroxides	$\text{Sn}(\text{OH})_2, 2\text{SnO} \cdot \text{H}_2\text{O}$	$\text{H}_2\text{SnO}_3, \text{H}_2\text{Sn}_2\text{O}_5, 5\text{SnO}_2 \cdot 3\text{H}_2\text{O}$
Oxychloride	"	$\text{Sn}_2\text{O}_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$
Sulphides	$\text{SnS}$ , the trioxide	$\text{SnS}_2$ , the trioxide
Sulphites	$\text{SnSO}_3$	$\text{Sn}(\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$
Nitrite	$\text{Sn}(\text{NO})_2, 2\text{OH} \cdot \text{O}$	$\text{Sn}(\text{NO}_2)_4$
Phosphides ( $\text{Sn}_3\text{P}, \text{Sn}_2\text{P}$ )	Phosphite (molecular), Aracides ( $\text{Sn}_3\text{As}_2, \text{Sn}_2\text{As}_3, \text{SnAs}$ , Stannoxalates.	

## ORGANIC COMPOUNDS OF TIN

**Tin Tetramethyl or Tetramethyl Stannane.**<sup>1</sup>  $\text{Sn}(\text{CH}_3)_4$ , prepared by the interaction of tin-sodium alloy and methyl iodide, is an ethereal liquid of density 1.314 at 0° C., insoluble in water and boiling at 78° C. Some *tin trimethyl iodide*,  $\text{Sn}(\text{CH}_3)_3\text{I}$ , boiling at 170° C. and having a density of 2.143 at 0° C., is formed at the same time.<sup>2</sup> *Tin dimethyl di-iodide*,  $\text{Sn}(\text{CH}_3)_2\text{I}_2$ , formed by heating sheet-tin with methyl iodide at 150° C., forms yellow monoclinic crystals which melt at 30° C., forming a liquid which boils at 228° C. (Cahours). To this compound there correspond the *oxide*  $\text{Sn}(\text{CH}_3)_2\text{O}$ , *dimethyl stannone*, the *chloride*  $\text{Sn}(\text{CH}_3)_2\text{Cl}_2$ , melting at 90° C. and boiling at 188°-190° C., and the *sulphate*  $\text{Sn}(\text{CH}_3)_2\text{SO}_4$ .

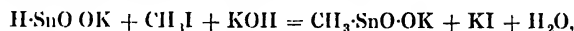
*Methyl stannic chloride*,  $\text{Sn}(\text{CH}_3)_4\text{Cl}_4$ , prisms melting at 53° C.; *methyl stannic bromide*,  $\text{Sn}(\text{CH}_3)_4\text{Br}_4$ ,<sup>3</sup> needles melting at 53° C.; *methyl stannic iodide*,  $\text{Sn}(\text{CH}_3)_4\text{I}_4$ , yellow prisms melting at 86.5° C., are formed by the action of the corresponding halogen hydracid on *methyl stannic acid*,  $\text{Sn}(\text{CH}_3)_4\text{O}(\text{OH})_2$ , and are converted into the latter substance by the action of ammonia. Methyl stannic acid, which may be regarded

<sup>1</sup> See Smith and Kipping, *Trans. Chem. Soc.*, 1912, 101, 2554.

<sup>2</sup> Ladenburg, *Annalen Suppl.*, 1872, 8, 75; Cahours, *Annalen*, 1860, 114, 372.

<sup>3</sup> Shukoff, *Ber.*, 1905, 38, 2691.

as *methyl stannonic acid*,  $\text{CH}_3\text{SnO}\cdot\text{OH}$ , is obtained by the action of methyl iodide on potassium stannite, thus <sup>1</sup>:



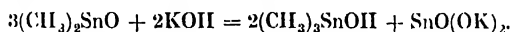
the resulting potassium salt being then decomposed by carbonic acid. When warmed with alkali solution, however, the potassium salt gradually produces dimethyl stannone and potassium stannate, thus:



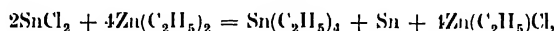
by a change analogous to that which acetate undergoes when heated:



and when dimethyl stannone is distilled with alkali it yields *trimethyl stannic hydroxide*,  $(\text{CH}_3)_3\text{Sn}\cdot\text{OH}$ , thus <sup>2</sup>:



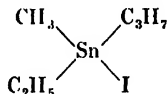
**Tin Tetra-ethyl**,  $\text{Sn}(\text{C}_2\text{H}_5)_4$ , prepared from zinc ethyl and stannous chloride,<sup>3</sup> according to the following reaction:



is a combustible liquid having a density of 1.187 at 23° C.; it is insoluble in water and boils at 181° C. *Tin tri-ethyl iodide*,  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{I}$ , exists, to which there correspond an oxide, hydroxide, and various salts; likewise the *di-ethyl di-iodide*,  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{I}_2$ , and salts such as sulphate, nitrate, acetate. The ethyl stannic compounds resemble those of methyl described above.<sup>4</sup>

**Tin Tri-ethyl**,  $[\text{Sn}(\text{C}_2\text{H}_5)_3]_2$ , an analogue of ethane, is formed when the iodide  $\text{Sn}(\text{C}_2\text{H}_5)_3\text{I}$  is distilled with sodium<sup>5</sup>; *tin di-ethyl*,  $\text{Sn}_2(\text{C}_2\text{H}_5)_4$ , an analogue of ethylene, is also known.

There are a few points of general interest connected with some of the above compounds. Methyl-ethyl-n-propyl stannic iodide.



was resolved by Pope and Peachey<sup>6</sup> into optically active components. Trimethyl stannic hydroxide,  $\text{Sn}(\text{CH}_3)_3\text{OH}$ , behaves as a very weak electrolyte, though it is a somewhat stronger base than aniline.<sup>7</sup> Di-ethyl stannic sulphate,  $\text{Sn}(\text{C}_2\text{H}_5)_2\text{SO}_4$ , shows a molecular weight in aqueous solution by the cryoscopic method, of 185 to 191, instead of 273, which the above formula would indicate, whence it is concluded that this salt is largely ionised in such solution.<sup>8</sup>

<sup>1</sup> G Meyer, *Ber.*, 1883, 16, 1442. Pfeiffer and Lehnardt, *Ber.*, 1903, 36, 1054

<sup>2</sup> Cahours, *Annalen*, 1860, 114, 375

<sup>3</sup> Frankland and Lawrence, *Trans. Chem. Soc.*, 1879, 35, 130

<sup>4</sup> Pfeiffer, *Ber.*, 1902, 35, 3303

<sup>5</sup> Ladenburg, *Annalen Suppl.*, 1872, 8, 75.

<sup>6</sup> Pope and Peachey, *Proc. Chem. Soc.*, 1900, 16, 42, 116

<sup>7</sup> Bredig, *Zeitsch. physikal. Chem.*, 1893, 11, 829. 1894, 13, 289

<sup>8</sup> Werner, *Zeitsch. anorg. Chem.*, 1898, 17, 91

## TIN AND THE HALOGENS

**Stannous Fluoride,  $\text{SnF}_2$ ,** is formed when the metal or the monoxide is dissolved in hydrofluoric acid, and is obtained on evaporation of the solution in white, monoclinic prisms,<sup>1</sup> stable in air and completely soluble in water. Stannous fluoride appears to combine with hydrofluoric acid and alkali fluorides forming complex acids and salts of the types  $\text{HSnF}_3$  and  $\text{H}_2\text{SnF}_4$ .<sup>2</sup>

**Stannic Fluoride,  $\text{SnF}_4$ ,** has been prepared by the interaction of stannic chloride and anhydrous hydrogen fluoride at high temperature.<sup>3</sup> It is a snow-white, crystalline, hygroscopic substance, which has a density of 1.78 at 19° C., and boils at 705° C. but sublimes below this temperature. It dissolves in water with evolution of heat, forming a solution from which hydrated stannic oxide separates on heating or allowing to stand. A solution, which decomposes similarly, is obtained by dissolving the hydrated oxide in hydrofluoric acid. Stannic fluoride combines with ammonia and other bases, and also with alkali and other fluorides to form stannifluorides of the type  $\text{M}_2\text{SnF}_6$ .

Stannic fluoride<sup>4</sup> forms with ammonia at 13° C. the white solid  $\text{SnF}_4 \cdot \text{NH}_3$ , which can be heated to 100° C. with loss of very little ammonia; the compound  $\text{SnF}_4 \cdot 2\text{NH}_3$  is formed when stannic fluoride and ammonia are heated in a sealed tube at 120–130° C. Both compounds dissolve in water, but their solutions gradually decompose. Aniline, pyridine, and quinoline also form additive compounds with stannic fluoride.

The stannifluorides were first investigated by Margnac.<sup>5</sup> They are isomorphous with the corresponding complex fluorides of silicon, titanium, germanium, and zirconium.

**Sodium Stannifluoride,  $\text{Na}_2\text{SnF}_6$ ,** is obtained by concentrating a mixed solution of hydrofluoric acid and sodium stannate. It is soluble in 19 to 20 parts of water at 20° C. and may be heated strongly without decomposition.

**Potassium Stannifluoride,  $\text{K}_2\text{SnF}_6 \cdot \text{H}_2\text{O}$ ,** is obtained similarly to the sodium salt, or by adding potassium fluoride solution to stannic chloride.<sup>6</sup> It is known in two forms, in octahedra and in leaflets. The former is the less soluble and more stable form at ordinary temperature, both forms are much more soluble in hot than in cold water. Hydrofluoric acid is evolved when this compound is treated with concentrated sulphuric acid.

The salts  $\text{K}_2\text{SnF}_6 \cdot \text{KF} \cdot \text{HF}$  and  $\text{K}_2\text{SnF}_6 \cdot \text{KF} \cdot 3\text{HF}$  have been obtained by employing excess of hydrofluoric acid.

**Ammonium Stannifluoride,  $(\text{NH}_4)_2\text{SnF}_6$ ,** was obtained by Margnac<sup>5</sup> by decomposing the lead or silver salt with ammonium chloride or sulphate. It crystallises in rhombohedra. The salt  $(\text{NH}_4)_2\text{SnF}_6 \cdot 2\text{NH}_4\text{F}$  has also been described. Stannifluorides of barium, strontium, calcium,

<sup>1</sup> Margnac, *Ann. des Mines*, 1857, v, 12; Fremy, *Ann. Chim. Phys.*, 1856, m, 47.<sup>1</sup>

<sup>2</sup> Wagner, *Ber.*, 1886, 19, 896.<sup>2</sup>

<sup>3</sup> Ruff, Plato, and Graf, *Ber.*, 1904, 37, 673.

<sup>4</sup> Wolter, *Chem. Zeit.*, 1912, 36, 165.

<sup>5</sup> Margnac, *Ann. des Mines*, 1859, [v], 15, 221.

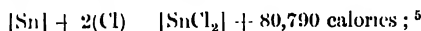
<sup>6</sup> Emich, *Monatsh.*, 1904, 25, 907.

magnesium, lead, manganese, zinc, cadmium, nickel, copper, and silver were also prepared by Marignac.

**Stannous Chloride**,  $\text{SnCl}_2$ , is formed by heating tin in hydrogen chloride gas, or by distilling the metal or its amalgam with the requisite amount of calomel or corrosive sublimate. It also results from the dehydration of the hydrate  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , by leaving it over sulphuric acid in a vacuum, or by heating it in a stream of hydrogen chloride gas. Anhydrous stannous chloride forms a transparent mass with a fatty lustre and a conchoidal fracture. It melts at  $250^\circ \text{C}$ ., and boils at  $606^\circ \text{C}$ .<sup>1</sup> or  $603^\circ \text{C}$ .<sup>2</sup> and is useful for obtaining a vapour bath of constant high temperature. Fused stannous chloride has remarkable reducing properties which have been studied by Sandonni and Aureggi.<sup>3</sup> Biltz and Meyer<sup>4</sup> found the vapour densities at various temperatures to be as follow:

Temperature $^\circ \text{C}$ . . . . .	639	678	699	759.6	790.2	1113
Vapour Density (Air = 1)	8.55	8.57	8.49	8.26	7.7	7.08
Vapour Density (H = 1)	123	123	122	119	111	102

The theoretical value for stannous chloride,  $\text{SnCl}_2$ , is 6.53 (Air = 1) or 94.0 (H = 1); hence it is inferred that some associated molecules,  $\text{Sn}_2\text{Cl}_4$ , exist in the state of vapour, but that they are dissociated as the temperature rises. When dissolved in methane, however, stannous chloride depresses the freezing-point of this substance by an amount which corresponds with the formula  $\frac{1}{2} \text{SnCl}_2$ . The heat of formation of stannous chloride from its elements is:



its specific heat between  $20^\circ \text{C}$ . and  $99^\circ \text{C}$ . is 0.1016.<sup>6</sup> Stannous chloride forms several compounds with ammonia.<sup>7</sup> Dry ammonia reacts with dry stannous chloride in a freezing mixture forming a yellow powder having the composition  $\text{SnCl}_2 \cdot 2\text{NH}_3$ , which blackens on exposure to light, and is decomposed by moisture into stannous oxide and ammonium chloride. At ordinary temperatures a mixture of the foregoing compound with  $\text{SnCl}_2 \cdot \text{NH}_3$ <sup>8</sup> is produced, whilst at  $100^\circ \text{C}$ . only the latter compound is formed. At  $120$ – $300^\circ \text{C}$ . a brownish red crystalline substance having the composition  $3\text{SnCl}_2 \cdot 2\text{NH}_3$  results; this is the most stable of the three compounds, and is only slowly decomposed by water.

Stannous chloride is said to form hydrates with one<sup>9</sup> and four<sup>10</sup> molecules of water, but the *dihydrate*  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is the compound best known. This compound, known commercially as *Tin Salt*, is prepared by dissolving tin in hydrochloric acid, and may also be obtained by dissolving the anhydrous salt in water, or stannous hydroxide in hydrochloric acid. It separates from its concentrated solution in transparent

<sup>1</sup> Biltz and Meyer, *Ber.*, 1888, 21, 22.

<sup>2</sup> McCrae, *Wied. Annalen*, 1895, 55, 95.

<sup>3</sup> Sandonni and Aureggi, *Gazzetta*, 1912, 42, [1], 227.

<sup>4</sup> Castoro, *Gazzetta*, 1898, 28, [u], 317.

<sup>5</sup> Thomsen, *Thermodynamische Untersuchungen*, Enke, (Stuttgart), 1906, p. 207.

<sup>6</sup> Regnault, *Ann. Chim. Phys.*, 1841, [iii], 1, 129.

<sup>7</sup> Sofianopoulos, *Compt. rend.*, 1911, 152, 865.

<sup>8</sup> Persoz, *Ann. Chim. Phys.*, 1830, [u], 44, 315.

<sup>9</sup> Ditté, *Compt. rend.*, 1883, 97, 42.

<sup>10</sup> Scheuter-Kestner, *Compt. rend.*, 1860, 50, 50.

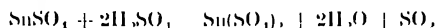
monoclinic prisms, or in octahedra, which have a density of 2.71, melt <sup>1</sup> at 40.5° C., and when further heated lose water and hydrogen chloride, leaving a basic chloride. This salt is very soluble in water; 100 grams of water dissolve 83.9 grams  $\text{SnCl}_2$  at 0° C., and 269.8 grams <sup>1</sup> at 15° C. When stannous chloride solution is diluted, hydrolysis takes place with separation of the insoluble basic chloride,  $2\text{Sn}(\text{OH})\text{Cl} \cdot \text{H}_2\text{O}$ , which redissolves in hydrochloric acid; the same precipitate is produced on account of atmospheric oxidation with the simultaneous formation of stannic chloride, thus



This precipitation may be prevented by keeping the acidified solution ever granulated tin, and also by adding tartaric acid, which forms a complex ion.

The action of excess of concentrated sulphuric acid on hydrated stannous chloride takes place in three successive stages <sup>4</sup>:

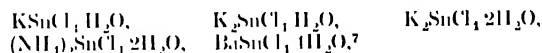
(i) Dehydration; (ii) liberation of hydrogen chloride between 20° C. and 90° C.; (iii) the reaction



between 130° C. and 200° C. The following reactions take place between stannous chloride and sulphurous acid at atmospheric temperatures <sup>1</sup>:

- (1) Primary  $3\text{SnCl}_2 + 6\text{HCl} + \text{H}_2\text{SO}_3 = 3\text{SnCl}_4 + 3\text{H}_2\text{O} + \text{H}_2\text{S}$ .
- (2) Consequent  $2\text{H}_2\text{S} + \text{H}_2\text{SO}_3 = 3\text{H}_2\text{O} + 3\text{S}$ .
- (3) Consequent  $2\text{H}_2\text{S} + \text{SnCl}_4 = 4\text{HCl} + \text{SnS}_2$ .
- (4) Consequent  $\text{H}_2\text{S} + \text{SnCl}_2 = 2\text{HCl} + \text{SnS}$ .
- (5) Retarding  $\text{SnCl}_4 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = \text{SnCl}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4$ .

Stannous chloride combines with hydrochloric acid and with potassium chloride and iodide in aqueous solution to form complex ions. This is proved by the reduction of electric conductivity.<sup>5</sup> The following complex salts, chlorostannites, have been isolated <sup>6</sup>:



as well as the free acid <sup>8</sup>  $\text{HSnCl}_3 \cdot 3\text{H}_2\text{O}$ , which melts at 27° C. Stannous chloride is readily soluble in alcohol; it also dissolves in acetone,<sup>9</sup> ether, and ethyl acetate.<sup>10</sup> An aqueous solution of stannous chloride absorbs free oxygen; the rate of absorption is roughly proportional to the concentration of hydrochloric acid present, and is much influenced by certain catalysers.<sup>11</sup> Connected with this

<sup>1</sup> Penny, *Trans. Chem. Soc.*, 1852, 4, 239.

<sup>2</sup> Engel, *Ann. Chem. Phys.*, 1889, [51] 17, 348.

<sup>3</sup> Michel and Kraft, *Ann. Chem. Phys.*, 1854, [m] 41, 478.

<sup>4</sup> Durant, *Trans. Chem. Soc.*, 1915, 107, 637.

<sup>5</sup> Young, *J. Amer. Chem. Soc.*, 1961, 23, 21.

<sup>6</sup> Renssen and Richardson, *Amer. Chem. J.*, 1892, 14, 89; but, according to Fujimura (*Mem. Coll. Sci. Kyoto*, 1914, 1, 63), the only existing potassium double chlorides are  $\text{KClSnCl}_2 \cdot \text{H}_2\text{O}$  and  $2\text{KClSnCl}_2 \cdot 2\text{H}_2\text{O}$ .

<sup>7</sup> Margnac, *Ann. Mines*, 1879, [v] 12, 1.

<sup>8</sup> Engel, *Bull. Soc. chim.*, 1888, [m] 150, 96.

<sup>9</sup> Naumann, *Ber.*, 1904, 37, 4312.

<sup>10</sup> Von Lasceyuski, *Ber.*, 1894, 27, 2285.

<sup>11</sup> Young, *J. Amer. Chem. Soc.*, 1901, 23, 119.

ability to absorb oxygen is the reducing action of stannous chloride, whereby it is converted into stannic salt. Stannous solutions are powerful reducing agents, and find varied application. Thus an acid solution of stannous chloride reduces ferric to ferrous chloride, cupric to cuprous chloride, and mercuric chloride to mercurous chloride and metallic mercury; it also reduces dilute nitric acid solution to hydroxylamine, bleaches indigo, and converts benzene diazonium chloride into phenyl hydrazine hydrochloride. Alkaline stannous solution reduces bismuthous hydroxide to the black suboxide,  $\text{Bi}_2\text{O}_3$ , and metallic bismuth. Tin-salt is used as a wool mordant for cochineal scarlet, for dyeing silk black, and for weighting silk. It is also employed for reducing indigo, in preparing "purple of Cassius,"<sup>1</sup> and in tinplating.

**Stannic Chloride,  $\text{SnCl}_4$ ,** was first obtained by Libavius in 1597, by distilling tin or its amalgam with corrosive sublimate. The liquid thus obtained was termed by its discoverer *Spiritus argenti vivi sublimati*, but was known later as *Spiritus fumans Libavii*. It was known in 1630 that a solution of this substance is obtained by dissolving tin in aqua regia; and a Dutchman named Drebbel discovered its value as a mordant by which the red colour of cochineal could be fixed on cloth.

Stannic chloride is prepared by passing chlorine over molten tin, tin-foil, or tin-plate. This latter method is employed in the recovery of tin from tin-plate waste (see p. 328). The reaction is accompanied by the evolution of heat and sometimes light. Stannic chloride may also be obtained by the action of chlorine on stannous chloride, and of chloroform vapour on the dioxide.<sup>2</sup> It is reduced to stannous chloride by hydrogen at  $1000^\circ \text{C}$ .<sup>3</sup> Stannic chloride is a thin, colourless, fuming liquid, which has a density of 2.2788 at  $0^\circ \text{C}$ .; it forms a solid at low temperature, which melts<sup>4</sup> at  $-33^\circ \text{C}$ ., and boils at  $113.89^\circ \text{C}$ . under 750 mm.,<sup>5</sup>  $114^\circ \text{C}$ . under 757 mm.,<sup>6</sup> and  $114.1^\circ \text{C}$ . under 760 mm. pressure<sup>7</sup>; its critical temperature is  $318.7^\circ \text{C}$ ., and critical pressure 36.95 atmospheres.<sup>8</sup> The heat of formation of this compound from its elements is 127,250 calories, and its heat of solution 29,920 calories.<sup>9</sup>

Stannic chloride dissolves very readily in alcohol, and also in ether, benzene, nitrobenzene, carbon disulphide, and other non-hydroxylic solvents. By the extent to which the freezing-points of such solvents are depressed when stannic chloride is dissolved in them, it is concluded that this compound undergoes molecular association in such solutions.<sup>10</sup> Although a solution of stannic chloride in benzene is non-conducting, and so contains no ions, it precipitates cupric chloride from a benzene solution of cupric oleate.<sup>11</sup>

Stannic chloride dissolves rhombic sulphur, yellow phosphorus, iodine, and bromine; with turpentine it reacts so vigorously as to set fire to the hydrocarbon. It dissolves in excess of water, forming

<sup>1</sup> See this series, vol. II.

<sup>2</sup> Benz, *Ber.*, 1906, 39, 249.

<sup>3</sup> Meyer and Keistern, *Ber.*, 1913, 46, 2882.

<sup>4</sup> Besson, *Compt. rend.*, 1889, 109, 940.

<sup>5</sup> Thorpe, *Trans. Chem. Soc.*, 1880, 37, 327.

<sup>6</sup> Walden, *Zeitsch. physikal. Chem.*, 1903, 43, 385.

<sup>7</sup> Young, *Trans. Chem. Soc.*, 1891, 59, 911.

<sup>8</sup> Young, *Phil. Mag.*, 1900, 50, 201.

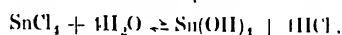
<sup>9</sup> Thomsen, *Thermochemische Untersuchungen*, Enke, (Stuttgart), 1906, p. 207.

<sup>10</sup> Kahlenberg and Lincoln, *J. Physical Chem.*, 1899, 3, 12.

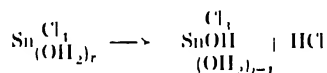
<sup>11</sup> Kahlenberg, *ibid.*, 1902, 6, 1.

a solution from which hydrated stannic oxide separates on boiling or standing; nevertheless it unites with smaller quantities of water to form various solid hydrates. Demarehy first observed, in 1770, that with one-third of its weight of water stannic chloride forms a crystalline mass, which was termed *butter of tin*. This hydrate, which is  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , is also called *orymuriate of tin*. Hydrates containing 3, 4, and 8 molecules of water are also known, and separate from the saturated solution with which they are in equilibrium at different temperatures. Thus  $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$  is stable up to  $19^\circ \text{C}$ .,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  is stable between  $19^\circ \text{C}$ . and  $56^\circ \text{C}$ .,  $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$  between  $56^\circ \text{C}$ . and  $63^\circ \text{C}$ .,  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$  between  $63^\circ \text{C}$ . and  $83^\circ \text{C}$ .<sup>1</sup>

The hydrolysis of stannic chloride proceeds according to the scheme:



the extent of the hydrolysis as measured by conductivity when equilibrium is attained depends, not only on the amount of water present, but also on the temperature, the raising of the temperature tending to retard the hydrolysis which is an exothermic reaction. The combination of stannic chloride with hydrochloric acid to form  $\text{H}_2\text{SnCl}_6$  also influences the equilibrium,<sup>2</sup> the conductivity being less than corresponds to the hydrochloric acid formed by hydrolysis. It has been shown by Pfeiffer<sup>3</sup> that the first product of the hydrolysis of a 50 per cent. solution of stannic chloride, externally cooled by ice, is the hydroxytrichloride  $\text{SnCl}_3\text{OH}$ , since the compound  $\text{SnCl}_3\text{OH} \cdot \text{H}_2\text{O}$  ( $\text{C}_2\text{H}_5\text{O}$ )<sub>2</sub> can be isolated after shaking out with ether. Pfeiffer suggests that hydrolysis proceeds according to the scheme:



Alcoholysis yields the compound  $\text{SnCl}_3\text{OC}_2\text{H}_5$ .<sup>4</sup>

The hydroxychloride  $\text{SnCl}_3\text{OH} \cdot 2\text{H}_2\text{O}$  may be written  $[\text{Sn} \begin{array}{c} \text{Cl}_3 \\ (\text{OH})_1 \end{array}] \cdot 2\text{H}_2\text{O}$  according to Werner's<sup>5</sup> system, so as to correspond with the acid  $[\text{SnCl}_6]\text{H}_2$ , to which also the hydrated potassium stannate  $\text{SnO}_3\text{K}_2 \cdot 3\text{H}_2\text{O}$  or  $[\text{Sn(OH)}_6]\text{K}_2$  appears to be related.

Stannic chloride forms various additive compounds. Thus with ammonia it yields a soluble, white powder, which according to Rose,<sup>7</sup> is  $\text{SnCl}_4 \cdot 2\text{NH}_3$ . Persoz, however, obtained a solid of the composition  $\text{SnCl}_4 \cdot 4\text{NH}_3$ , which could be sublimed unchanged in an atmosphere of hydrogen.<sup>8</sup> The compound with phosphine,  $3\text{SnCl}_4 \cdot 2\text{PH}_3$ , is a yellow, fuming solid.<sup>9</sup> With sulphur tetrachloride, stannic chloride forms the compound  $\text{SnCl}_4 \cdot 2\text{SCl}_2$ ,<sup>10</sup> which is also obtained in yellow crystals by

<sup>1</sup> Meyerhoffert, *Full. Soc. chim.*, 1801 [iii] 6, 83.

<sup>2</sup> Kowalevsky, *Zetsch. anorg. Chem.*, 1900, 23, 1; see also Koldhausch, *Zetsch. physikal. Chem.*, 1900, 33, 273.

<sup>3</sup> Pfeiffer, *Ber.*, 1905, 38, 2466.

<sup>4</sup> Fischer, *Momentsh.*, 1881, 5, 127.

<sup>5</sup> Werner and Pfeiffer, *Zetsch. anorg. Chem.*, 1898, 17, 82. See this series vol. ix, where Werner's Theory is dealt with in detail.

<sup>6</sup> Bellucci and Parravano, *Zetsch. anorg. Chem.*, 1905, 45, 143.

<sup>7</sup> Rose, *Pogg. Annalen*, 1832, 24, 109.

<sup>8</sup> Persoz, *Ann. Chim. Phys.*, 1830, 44, 322.

<sup>9</sup> Rose, *Pogg. Annalen*, 1829, 24, 159.

<sup>10</sup> Rose, *ibid.*, 1837, 42, 517.



the action of chlorine on stannic sulphide; these melt below  $30^{\circ}\text{C}$ . and decompose above  $10^{\circ}\text{C}$ . With phosphorus pentachloride the compound  $\text{SnCl}_4\cdot\text{PCl}_5$ <sup>1</sup> results: it forms colourless, glistening crystals, which fume strongly in the air and have a pungent odour; whilst with phosphoryl chloride the crystalline compound  $\text{SnCl}_4\cdot\text{POCl}_3$ , melting at  $58^{\circ}\text{C}$ . and distilling at  $180^{\circ}\text{C}$ ., is formed.<sup>1</sup>

Stannic chloride combines with dry nitrous fumes to form  $\text{SnCl}_4\cdot\text{N}_2\text{O}_3$ , a yellow amorphous mass; and when this substance is sublimed, or the dry vapours from aqua regia are passed into the chloride,  $\text{SnCl}_4\cdot 2\text{NOCl}$  is formed, and crystallises in shining octahedra; if, however, nitrogen peroxide is passed into a chloroform solution of stannic chloride the compound  $3\text{SnCl}_4\cdot\text{N}_2\text{O}_3$  is produced<sup>2</sup>; and when a chloroform solution of nitrogen sulphide is added to a similar solution of stannic chloride, red crystals of  $\text{SnCl}_4\cdot 2\text{N}_2\text{S}_4$  separate.<sup>3</sup> With sulphur trioxide the white solid  $\text{SnCl}_4\cdot\text{SO}_3$  is formed.<sup>4</sup>

Stannic chloride is employed in dyeing, as a mordant, and for weighting silk. Formerly a preparation known as *tin-composition*, *physic*, or *dyers' spirit* was employed; this was made by dissolving tin with common salt or sal ammoniac in nitric acid, or the metal alone in aqua regia; but now the pentahydrate,  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ , oxymuriate of tin, is generally used.

**The Stannichlorides or Chlorostannates.**—Chlorostannic acid,  $\text{H}_2\text{SnCl}_6$ , exists, and from it are derived a number of salts, the stannichlorides.

*Chlorostannic Acid*,  $\text{H}_2\text{SnCl}_6\cdot 6\text{H}_2\text{O}$ , is formed when the solid pentahydrate  $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ , or a concentrated solution of the chloride is saturated with hydrogen chloride gas. It separates on cooling the liquid to  $0^{\circ}\text{C}$ . in thin plates, which melt at about  $20^{\circ}\text{C}$ .<sup>5</sup> There is a marked similarity between this acid and its salts and chloroplatinic acid,  $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ , and its salts,<sup>6</sup> though the latter acid and its salts are the more stable.

*Sodium Stannichloride*,  $\text{Na}_2\text{SnCl}_6\cdot 5\text{H}_2\text{O}$ , crystallises in prisms when the concentrated solutions of the constituent salts are mixed together, the *potassium salt*  $\text{K}_2\text{SnCl}_6$  crystallises in anhydrous regular octahedra, with which the *ammonium salt*  $(\text{NH}_4)_2\text{SnCl}_6$  is isomorphous. This latter salt was formerly used by dyers, and was named *pink salt*, because of its use as a mordant for madder-red colours; it dissolves in 3 parts of water at  $14.5^{\circ}\text{C}$ ., and from its dilute solution stannic hydroxide separates on boiling. A large number of stannichlorides have been prepared<sup>7</sup> containing various amounts of water of crystallisation; the chlorides of barium, cadmium, copper, silver, lead, and thallium, however, appear not to combine with stannic chloride.

**Stannous Bromide**,  $\text{SnBr}_2$ , is prepared by allowing molten tin to cool to  $200^{\circ}\text{C}$ ., powdering the metal in a mortar, and dissolving the powder in concentrated hydrobromic acid solution.<sup>8</sup> It may also be

<sup>1</sup> Casselmann, *Annalen*, 1872, 83, 257.

<sup>2</sup> Thomas, *Compt. rend.*, 1896, 122, 32.

<sup>3</sup> Davis, *Trans. Chem. Soc.*, 1900, 89, 1570.

<sup>4</sup> Rose, *Pogg. Annalen*, 1838, 44, 320.

<sup>5</sup> Engel, *Compt. rend.*, 1886, 103, 213; Seubert, *Ber.*, 1887, 20, 793.

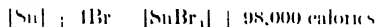
<sup>6</sup> Bellucci and Paraviano, *Zeitsch. anorg. Chem.*, 1905, 145, 142.

<sup>7</sup> Biron, *J. Russ. Chem. Soc.*, 1901, 36, 489, and *Abh. R. Acad. Lincei*, 1904, [v], 13, ii, 307.

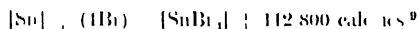
<sup>8</sup> Freyer and V. Meyer, *Zeitsch. anorg. Chem.*, 1892, 2, 1.

obtained by heating tin in hydrogen bromide gas, or distilling the metal with mercuric bromide. It is a pale yellow crystalline mass, of density 5.1, which melts at 215.5° C., and boils at 619° C. The heat of formation of the solid from tin and liquid bromine is 61,500 calories.<sup>1</sup> Stannous bromide forms a hydrate with water which is probably  $\text{SnBr}_2 \cdot \text{H}_2\text{O}$ <sup>2</sup>; it is, however, hydrolysed by much water with separation of a white oxybromide. With ammonium bromide, stannous bromide forms the complex salt  $(\text{NH}_4)_2\text{SnBr}_4 \cdot \text{H}_2\text{O}$ <sup>3</sup> or  $(\text{NH}_4)_2\text{SnBr}_4 \cdot 2\text{H}_2\text{O}$ ,<sup>4</sup> and also  $\text{NH}_4\text{SnBr}_4 \cdot \text{H}_2\text{O}$ , whilst with ammonium chloride  $(\text{NH}_4)_2\text{SnBr}_4 \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$  and with potassium bromide  $\text{K}_2\text{SnBr}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{KSnBr}_4 \cdot \text{H}_2\text{O}$  result.

**Stannic Bromide**,  $\text{SnBr}_4$ , is formed from its elements, which combine with evolution of light and heat.<sup>5</sup> It is best prepared, according to Lorenz,<sup>6</sup> by dropping bromine from a capillary tube on to strips of tin contained in a distilling flask, removing excess of bromine by warming the flask, and then distilling the bromide, which so obtained, is a snow-white crystalline mass. The physical constants of this substance are not known with certainty, owing to the different values obtained by different observers. Cannelley and O'Shea<sup>7</sup> determined the vapour density to be 229 (theory requires 219 when  $\text{H} = 1$ ), and the melting-point 30° C., whilst for the latter, Raymann and Preis<sup>8</sup> found 33° C., and Gaidh<sup>9</sup> 29.15° C. The boiling-point is 203.3° C. (Raymann and Preis), or 201° C. (Cannellcy and O'Shea, Lorenz, Neumann) and the density of the liquid at 33° C. is 3.319 (Raymann and Preis), and at 39° C. 3.322 (Bodeker).<sup>10</sup> Berthelot<sup>1</sup> estimated the heat of formation of stannic bromide to be .



and



Because it has a high molecular depression and a convenient melting-point, this substance has been employed by Gaidh in cryoscopic determinations,<sup>7</sup> the molecular depression being estimated to be 280. According to Tolluezo<sup>10</sup> however, the value should be 305.

Stannic bromide fumes in the air, and is readily soluble in cold water. From this solution the hydroxide separates slowly on standing and quickly on boiling. Nevertheless the hydrate  $\text{SnBr}_4 \cdot \text{H}_2\text{O}$  is obtained when an aqueous solution of the anhydrous bromide is evaporated over sulphuric acid (Raymann and Preis).

With ammonia stannic bromide forms the additive compound  $\text{SnBr}_4 \cdot 2\text{NH}_3$  (Raymann and Preis).

**Bromostannic Acid** exists. According to Raymann and Preis<sup>8</sup> it is  $\text{H}_2\text{SnBr}_6 \cdot 8\text{H}_2\text{O}$  but Seubert<sup>11</sup> gives it the formula  $\text{H}_2\text{SnBr}_6 \cdot 7\text{H}_2\text{O}$ . Alkali stannibromides are known.

<sup>1</sup> Berthelot, *Thermochimie*, 1897, 2, 1-6.

<sup>2</sup> Raymann and Preis, *Londan*, 1884, 223, 424.

<sup>3</sup> Remson and Richardson, *Amer. Chem. J.*, 1892, 14, 89.

<sup>4</sup> Raymann and Preis, *Londan*, 1884, 223, 323.

<sup>5</sup> Lorenz, *Zeitschrift Chem.*, 1895, 9, 365.

<sup>6</sup> Cannelley and O'Shea, *Trans. Chem. Soc.*, 1878, 33, 55.

<sup>7</sup> Gaidh, *Gaz. (ita)*, 1898, 28, [1, 23].

<sup>8</sup> Bodeker, *Die Beziehungen zwischen Dichte und Zersetzung bei festen und liquiden Stoffen* (Leipzig, 1860).

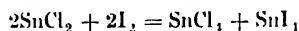
<sup>9</sup> Note: Square brackets indicate the solid state, round brackets the gaseous state, no brackets the liquid state.

<sup>10</sup> Tolluezo, *Bull. Acad. Sci. Cracoe*, 1911, 1, see also Tolluezo and Meyer, *Chem. Zentr.*, 1910, ii, 1021.

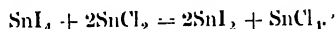
<sup>11</sup> Seubert, *Ber.*, 1887, 20, 793.

**Stannous Iodide**,  $\text{SnI}_2$ , is obtained by adding potassium iodide in slight excess to a concentrated solution of stannous chloride, or by the action of hydriodic acid on tin; it crystallises in orange-red octahedra, which may be obtained by melting the compound, or evaporating its solution in carbon disulphide; but it is probably dimorphous. It melts at  $320^\circ \text{C.}$ , and boils at  $720^\circ \text{C.}$ <sup>1</sup> The dihydrate  $\text{SnI}_2 \cdot 2\text{H}_2\text{O}$  is said to exist; 100 parts of water dissolve 0.98 parts of anhydrous stannous iodide at  $20^\circ \text{C.}$ , and 4.03 parts at  $100^\circ \text{C.}$ <sup>2</sup> It is much more soluble in hydriodic acid and alkali halide solutions, owing to the formation of a complex acid or salts.

When a solution of stannous chloride is titrated with iodine it is sometimes assumed that an additive reaction takes place with the formation of stannic iodochloride,  $\text{SnCl}_2\text{I}_2$ , but most likely a mixture of stannic chloride and iodide is produced thus:



stannic iodide is, however, reduced to stannous iodide by excess of stannous chloride, thus:



Stannous iodide combines with hydrogen iodide to form *iodostannous acid*,  $\text{HSnI}_3$ ; and unstable, pale yellow needles of this substance separate at  $0^\circ \text{C.}$  from a saturated solution of stannous iodide in hydriodic acid.<sup>3</sup> To this acid there correspond the *iodostannites* or *stannio-iodides*:  $\text{NaSnI}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{KSnI}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{NH}_4\text{SnI}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Sr}(\text{SnI}_3)_2$ , and  $\text{Ba}(\text{SnI}_3)_2$ , which separate when the corresponding saline iodides are added to concentrated stannous chloride solution.

Stannous iodide combines with ammonia to form the compound  $\text{SnI}_2 \cdot 2\text{NH}_3$ ,<sup>5</sup> which is yellow.<sup>6</sup>

**Stannic Iodide**,  $\text{SnI}_4$ , is formed from its elements, and is conveniently prepared by bringing together a carbon disulphide solution of iodine and metallic tin.<sup>7</sup> Carbon tetrachloride may, however, be advantageously substituted for carbon disulphide, owing to the fact that stannic iodide is much more soluble in this solvent at its boiling-point than at ordinary temperature, and, therefore, separates on cooling.<sup>8</sup> The iodide may also be obtained by precipitating a concentrated solution of stannic chloride with potassium iodide. It is a bright red, crystalline powder consisting of regular octahedra;<sup>9</sup> after sublimation, however, it appears in yellowish red needles. This compound melts at  $113.5^\circ \text{C.}$ , and boils at  $340^\circ \text{C.}$ , though it is said to sublime<sup>10</sup> at  $180^\circ \text{C.}$  It may be dissolved in carbon disulphide, alcohol, ether, chloroform, benzene, and arsenic tribromide. Cryoscopic determinations of the molecular weight of stannic iodide in the last-named

<sup>1</sup> Reinders and de Lange, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 474.

<sup>2</sup> Young, *J. Amer. Chem. Soc.*, 1897, **19**, 515.

<sup>3</sup> Young and Adams, *J. Amer. Chem. Soc.*, 1897, **19**, 515.

<sup>4</sup> Young, *ibid.*, 1897, **19**, 851.

<sup>5</sup> Rammelsberg, *Pogg. Annalen*, 1839, **48**, 151.

<sup>6</sup> Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.

<sup>7</sup> Personne, *Compt. rend.*, 1862, **54**, 216.

<sup>8</sup> McDermott, *J. Amer. Chem. Soc.*, 1911, **33**, 1963.

<sup>9</sup> Reigers, *Zeitsch. anorg. Chem.*, 1894, **5**, 211.

<sup>10</sup> Henry, *Phil. Trans.*, 1845, **135**, 363.

solvent yield abnormal results, of which various explanations have been given.<sup>1</sup>

Stannic iodide does not give a clear solution with water on account of hydrolysis; it forms with ammonia three additive compounds:  $\text{SnI}_4 \cdot 3\text{NH}_3$ ,  $\text{SnI}_4 \cdot 4\text{NH}_3$ ,  $\text{SnI}_4 \cdot 6\text{NH}_3$  (Persimon), which are produced by the action of ammonia on a solution of the iodide in carbon disulphide or ether. The first compound is yellow, the other two are white. They are all volatile and are decomposed by water into ammonia, ammonium iodide, and stannic oxide. The compound  $\text{SnI}_4 \cdot 8\text{NH}_3$  has also been prepared.<sup>2</sup>

*Iodostannic Acid* cannot be formed in aqueous solution on account of the hydrolysis of stannic iodide, which is much more complete than that of the chloride. Pyridine stannic iodide,  $(\text{C}_5\text{H}_5\text{NH})_2\text{SnI}_6$ , is formed in bluish black needles when an alcoholic solution of pyridine hydroiodide is added to a solution of stannic iodide in alcoholic hydrogen iodide. The quinoline salt is similarly obtained.<sup>3</sup>

**Mixed Stannic Halides.** Stannic chlorobromide,  $\text{SnCl}_2\text{Br}_2$ , was described by Ladenburg,<sup>4</sup> and the three compounds,  $\text{SnCl}_3\text{Br}$ ,  $\text{SnCl}_2\text{Br}_2$ , and  $\text{SnClBr}_3$ , by Besson;<sup>5</sup> whilst Lanoumand<sup>6</sup> supposed that he had obtained  $\text{SnCl}_3\text{I}$ ,  $\text{SnCl}_2\text{I}_2$ ,  $\text{SnClI}_3$ ,  $\text{SnBr}_3\text{I}$ ,  $\text{SnBr}_2\text{I}_2$ ,  $\text{SnBrI}_3$  by the interaction of stannous halides and appropriate halogens or halogen hydrides; but it has been shown by Auger,<sup>7</sup> by reference to their physical behaviour, that all these supposed compounds are probably mixtures.

Thus, mixtures of  $\text{SnBr}_3\text{I}$  and  $\text{SnI}_4$  show a normal freezing-point curve, with a eutectic point at the composition  $\text{SnBr}_3\text{I}_{0.8}$ ; and the supposed compound  $\text{SnBr}_2\text{I}_2$ , which melts at  $51^\circ\text{C}$ , is identical with an equimolecular mixture of  $\text{SnBr}_3\text{I}$  and  $\text{SnI}_4$ , and may be separated by ten fractional crystallisations into fractions melting at  $88^\circ\text{C}$ . and  $27^\circ\text{C}$ , having the compositions  $\text{SnBr}_3\text{I}_{1.2}$  and  $\text{SnBr}_3\text{I}_1$ , respectively.

Similarly the supposed compounds  $\text{SnBrI}_3$  and  $\text{SnBr}_3\text{I}$  may be partly resolved by crystallisation. Moreover, it is suggested that in all molten mixtures of the composition  $\text{SnBr}_3\text{I}_{1.2}$  the halogen atoms are perfectly mobile, and that the same is true for the chlorobromides and chloroiodides.

## TIN AND OXYGEN

**Stannous Oxide** (*Tin Monoxide*),  $\text{SnO}$ , may be prepared in several ways. It is obtained by heating a mixture of stannous chloride and sodium carbonate until it becomes black, then washing with water, and drying the residue with a gentle heat in a stream of carbon dioxide. It is also produced by igniting stannous oxalate out of contact with air, when it is obtained as an olive-green powder, and by precipitating stannous chloride solution with alkali, and boiling the hydrated oxide thus produced with dilute caustic potash solution, the anhydrous

<sup>1</sup> Tallorzo, *Bull. Acad. Sci. Croat.*, 1901, 1. Gault and Besson, *Ann. R. Acad. Sci. Madrid*, 1901, [13], 10, 255. Walden, *Zetsch. anorg. Chem.*, 1902, 29, 371.

<sup>2</sup> Ephraïm and Schmidt, *Ber.*, 1909, 42, 3850.

<sup>3</sup> Rosenbach and Aron, *Zetsch. anorg. Chem.*, 1904, 39, 170.

<sup>4</sup> Ladenburg, *Annalen Suppl.*, 1872, 8, 55.

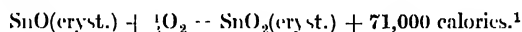
<sup>5</sup> Besson, *Compt. rend.*, 1897, 124, 684.

<sup>6</sup> Lanoumand, *J. Pharm.*, 1898 [vi], 8, 249, 1899, [vi], 10, 114.

<sup>7</sup> Auger, *Compt. rend.*, 1909, 149, 869.

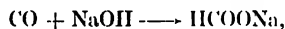
oxide thus formed crystallises in microscopic cubes or octahedra. A crystalline form of the oxide is also obtained by digesting a nearly saturated solution of stannous oxide in acetic acid of density 1.06 at 56° C. This form of the oxide is red, but quickly turns black on exposure to sunlight.

The black amorphous oxide easily dissolves in hydrochloric acid forming stannous chloride, and burns when heated in the air forming the dioxide :



**Stannous Hydroxide.**—The white precipitate obtained by adding alkali hydroxide or carbonate solution to stannous chloride is said not to be  $\text{Sn}(\text{OH})_2$ , but to have the composition  $2\text{SnO} \cdot \text{H}_2\text{O}$ .<sup>2</sup> If this precipitate is heated above 80° C. it loses water, and passes into the anhydrous oxide. The hydroxide dissolves in excess of alkali producing a solution of alkali stannite, which, according to Hantzsch,<sup>3</sup> is not  $\text{Sn}(\text{ONa})_2$ , but  $\text{H} \cdot \text{SnO} \cdot \text{ONa}$ , there being no ground for assuming the existence of  $\text{SnO}_2^{--}$  ions. Thus tin becomes quadrivalent in stannites, and the hydroxide is a feeble acid of the type of formic acid.

This conclusion in regard to constitution, which applies to the hydroxides of zinc, glucinum, lead, tin, and germanium, is based upon measurements of the conductivities of their alkaline solutions, and the rate at which these solutions hydrolyse ethyl acetate. The metals are named in the order of increasing acidic strength of their hydroxides. It is interesting to remember that carbon monoxide combines similarly with alkali :



and that there are other acids probably constituted in an analogous manner, so that the maximum valency of the nuclear atoms is reached, e.g.  $\text{H}_2\text{SO}_3\text{OH}$ ,  $\text{H}_2\text{POOH}$ , and  $\text{HPO}(\text{OH})_2$ . It may be remarked, however, that this constitution of stannites involves the union of a hydrogen and a tin atom, otherwise unknown. The reducing action of sodium stannite solution has been studied by Goldschmidt and Eckardt,<sup>4</sup> who agree with Hantzsch in regard to the constitution of this salt.

**Stannic Oxide (Tin Dioxide),**  $\text{SnO}_2$ , occurs in crystalline and amorphous forms. As regards its crystalline forms, it is trimorphous, existing in tetragonal, hexagonal, and rhombic crystals. Native stannic oxide, *cassiterite* or *tinstone*, occurs in tetragonal crystals, which when quite pure are colourless and transparent, but are generally yellow, green, brown, or black, from the presence of oxide of iron or other impurity.

Tinstone may owe its origin to the hydrolysis of stannic fluoride or chloride by water-vapour, i.e. to so-called pneumatolytic action. Stannic oxide is infusible before the blowpipe, but it can be melted, and even vaporised in the electric furnace. Its melting-point<sup>5</sup> is estimated to be 1127° C. Various values have been obtained for the density of crystallised stannic oxide, owing to varying degrees of purity of the substance ; the mean value is 6.9 at 15° C.

<sup>1</sup> Mixer, *Amer. J. Sci.*, 1909, [iv], 27, 229.

<sup>2</sup> Schaffner, *Annalen*, 1844, 51, 468.

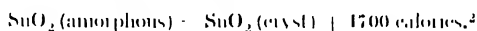
<sup>3</sup> Hantzsch, *Zeitsch. anorg. Chem.*, 1902, 30, 289.

<sup>4</sup> Goldschmidt and Eckardt, *Zeitsch. physikal. Chem.*, 1906, 56, 385.

<sup>5</sup> Cussak, *Proc. Roy. Irish Acad.*, 1896-1898, [iii], 4, 399.

Amorphous stannic oxide may be obtained in various ways. If tin is heated in the air it takes fire when near its boiling-point and burns with a bright flame, forming the dioxide. Obtained in this way stannic oxide was originally named *flores Jovis*, whilst the oxide formed by the superficial oxidation of molten tin, which is grey because it contains particles of finely divided metal, has been called *flores stanni*. Stannic oxide is also formed when stannous oxide or oxalate, or either of the sulphides is roasted in the air, and by the ignition of the hydrated oxide formed by the action of nitric acid on the metal, as well as in other ways to be noticed later. It is likewise obtained during the electrolysis of a solution of sodium or potassium chloride with a tin plate as anode, and a platinum plate as cathode.<sup>1</sup> Amorphous stannic oxide is a white or cream-coloured powder, which turns yellow and brown when heated, but fades to its original colour on cooling.

The amorphous oxide is converted into the crystalline form of cassiterite when it is heated in a current of hydrogen chloride gas. The thermal relationship between crystalline and amorphous stannic oxide is represented by the equation



The anhydrous oxide is quite insoluble in water, and is not attacked by concentrated acids, except sulphuric acid, with which it forms an unstable sulphate. Fusion with potassium hydrogen sulphate also dissolves the oxide. A method of treatment, however, which is convenient in qualitative analysis, is to fuse the oxide with a mixture of sodium carbonate and flowers of sulphur. The fused mass dissolves in water, yielding a solution of sodium thioantimonate, from which dilute acid precipitates stannic sulphide. This can then be dissolved in concentrated hydrochloric acid. Stannic oxide is employed, under the name of *putty powder*, for polishing glass and metal.

**Hydrated Stannic Oxide: the Stannic Acids.** Berzelius,<sup>3</sup> in 1817, recorded the existence of two forms of hydrated stannic oxide, or stannic acid, of the composition represented by the empirical formula  $\text{H}_2\text{SnO}_3$ ; and this was the first known example of isomerism. The one form is obtained by precipitation from stannic salts or stannate solutions, the other by heating tin with moderately concentrated nitric acid. The two forms differ in solubility, and especially in the composition of the salts they yield with alkalis: salts of the former acid contain one equivalent of stannic oxide, and are of the type  $\text{M}'_2\text{SnO}_3$ ; salts of the latter have five equivalents of the oxide and are, therefore, of the type  $\text{M}'_5\text{Sn}_5\text{O}_{15}$ .

The two acids have been named stannic and metastannic acid respectively, but this nomenclature is misleading, since  $\text{H}_2\text{SnO}_3$  is properly metastannic acid. They are better known as  $\alpha$ - and  $\beta$ -stannic acids; the term *meta* may then be employed in addition where it is appropriate. According to Mecklenburgh, the  $\alpha$ - and  $\beta$ -stannic acids are to be regarded merely as colloidal substances, differing in the size of their particles.<sup>4</sup>

<sup>1</sup> Lorenz, *Zeitsch. anorg. Chem.*, 1896, 12, 136.

<sup>2</sup> Minter, *Amer. J. Sci.*, 1909, [iv], 27, 229.

<sup>3</sup> Berzelius, *Annalen*, 1817, [ii], 5, 119.

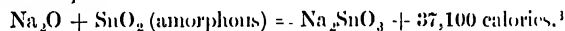
<sup>4</sup> Mecklenburgh, *Zeitsch. anorg. Chem.*, 1909, 64, 308, 4912, 74, 207, 1913, 84, 121.

**$\alpha$ -Stannic Acid and its Salts.**— $\alpha$ -Stannic acid is obtained as a white powder by precipitating stannic chloride with ammonia, or by means of calcium carbonate; by adding dilute acid to the solution of a stannate, or ammonium chloride to the same solution, since ammonium stannate, like the corresponding silicate, is immediately hydrolysed by water. The addition of sodium sulphate to stannic chloride solution also produces a precipitate of stannic hydroxide, since stannic sulphate is unstable, and is hydrolysed. These two latter reactions furnish an interesting example of the behaviour of an amphoteric hydroxide, since in the former case the hydroxide is precipitated as a weak acid, in the latter case as a weak base. When the precipitate is air-dried it contains 22.5 per cent. of water,<sup>1</sup> which is rather more than corresponds to the formula of the ortho-hydroxide,  $\text{Sn}(\text{OH})_4$ . When dried *in vacuo*, or at  $100^\circ \text{C}$ ., the hydroxide has approximately the composition of the meta-acid  $\text{H}_2\text{SnO}_3$ .<sup>2</sup>

The precipitate before drying is slightly soluble in water, to which it imparts an acid reaction; it also dissolves in nitric, sulphuric, and hydrochloric acids, as well as in caustic soda. When the acid is dried it undergoes partial transformation into the  $\beta$  form, this also occurs under water, especially on heating.

The alkali  $\alpha$ -stannates can be obtained crystalline, and are soluble in water; other stannates are obtained from them by precipitation.

**Sodium Stannate.**  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , is obtained by fusing finely divided tinstone with caustic soda, or by heating tin with caustic soda and Chili saltpetre.



The trihydrated salt crystallises from aqueous solution, and is more soluble in cold than in hot water; from such solution deca-hydrated crystals,  $\text{Na}_2\text{SnO}_3 \cdot 10\text{H}_2\text{O}$ , can also be obtained. When the trihydrate is heated it loses all its water, and the anhydrous stannate thus produced does not dissolve unchanged in water and cannot be rehydrated. This salt is used in calico printing, and is called *preparing salts*.

**Potassium Stannate.**  $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , is prepared similarly to the sodium salt. It cannot, however, be completely dehydrated by heating, but decomposes, forming potassium hydroxide and stannic acid.<sup>4</sup> Consequently the water present is water of hydroxylation rather than of hydration, and thus and other salts are derived from hexahydroxystannic acid,  $\text{H}_2\text{Sn}(\text{OH})_6$ , which is analogous to hexahydroxyplatonic acid,  $\text{H}_2\text{Pt}(\text{OH})_6$ . This conclusion is confirmed by the fact that insoluble stannates obtained by double decomposition contain the same proportion of water. Thus precipitated lead stannate is  $\text{PbSnO}_3 \cdot 3\text{H}_2\text{O}$ ,<sup>5</sup> and may be formulated  $\text{PbSn}(\text{OH})_6$ . This constitution relates hexahydroxystannates to the stannic chlorides  $\text{M}'_2\text{SnCl}_6$ , which are analogous to the platinum chlorides  $\text{M}'_2\text{PtCl}_6$ . No orthostannates have hitherto been recognised, but Hedvall<sup>6</sup> has prepared cobaltous orthostannate,  $\text{Co}_2\text{SnO}_4$ , by fusing cobaltous and stannic oxides with potassium chloride at  $1100^\circ \text{C}$ . or  $1300^\circ$ – $1400^\circ \text{C}$ ., and dissolving out

<sup>1</sup> Warren, *Chem. News*, 1890, 62, 216.

<sup>2</sup> Weber, *Pogg. Annalen*, 1861, 122, 358.

<sup>3</sup> Mixer, *Amer. J. Sci.*, 1909, [iv], 27, 229.

<sup>4</sup> Bellucci and Parravano, *Atti R. Accad. Lincei*, 1904, [v], 13, n. 324.

<sup>5</sup> Bellucci and Parravano, *Atti R. Accad. Lincei*, 1904, [v], 13, n. 339.

<sup>6</sup> Hedvall, *Arkiv. Kem. Min. Geol.*, 1914, 5, No. 18, 1.

the excess of stannic oxide by warm, dilute hydrochloric acid. The product is dark green, and has a density of 6.30 at 18° C.

**$\beta$ -Stannic Acid and its Derivatives.** Boyle,<sup>1</sup> in 1670, stated that aqua fortis destroys more tin than it dissolves, and also observed that a solution of tin in the same liquid easily becomes gelatinous.<sup>2</sup> Kunkel<sup>3</sup> likewise recorded the fact that to dissolve tin the nitric acid employed must be cold, or calc. of tin would be precipitated. The explanation of these observations is that whilst tin dissolves slowly in very dilute nitric acid to produce stannous nitrate, the stannous nitrate first formed, when hot and more concentrated acid is employed, is very unstable and quickly decomposes, yielding the form of hydrated stannic oxide known as  $\beta$ -stannic acid. Probably  $\alpha$ -stannic acid is first produced from stannic nitrate, which then passes into the  $\beta$ -form. The product is, therefore, liable to contain both  $\alpha$ - and  $\beta$ -forms, and the pure  $\beta$ -acid is obtained by dissolving this product in sodium hydroxide solution, and then adding excess of concentrated soda, which precipitates sodium  $\beta$ -stannate whilst the  $\alpha$ -salt remains in solution. Pure  $\beta$ -stannic acid, or  $\beta$ -metastannic acid, is then obtained by decomposing the sodium salt with acid. It is also formed by the hydrolysis of its sodium salt at 60° C., and by boiling a dilute solution of stannic chloride, with or without the addition of nitric acid. Moreover, when a solution of  $\alpha$ -stannic acid in hydrochloric or hydrobromic acid is allowed to stand,  $\beta$ -stannic acid gradually separates as an opalescent precipitate and the process of transformation can be followed quantitatively.<sup>4</sup>

A hydrosol of stannic acid was obtained by Graham<sup>5</sup> by the dialysis of a mixture of stannic chloride and alkali, or of sodium stannate and hydrochloric acid. The liquid at first contained a gelatinous precipitate which gradually dissolved. The hydrosol was gelatinised by a trace of hydrochloric acid or of a salt, and on heating yielded colloidal  $\beta$ -stannic acid. Gelatinous, precipitated  $\beta$ -stannic acid has the empirical composition  $\text{SnO}_2 \cdot 11\text{H}_2\text{O}$ , when air-dried  $\text{SnO}_2 \cdot 21\text{H}_2\text{O}$ , and when dried in a vacuum,  $\text{SnO}_2 \cdot \text{H}_2\text{O}$ . These formulae do not, however, convey a just idea of the nature of the  $\beta$ -acid, which is gained from a study of its salts and other derivatives.

*Sodium  $\beta$ -stannate*, prepared by the action of cold sodium hydroxide solution on  $\beta$ -stannic acid, is a sparingly soluble crystalline powder, having the composition  $\text{Na}_2\text{Sn}_5\text{O}_{11} \cdot 11\text{H}_2\text{O}$ . Similarly the potassium salt is  $\text{K}_2\text{Sn}_5\text{O}_{11} \cdot 11\text{H}_2\text{O}$ . Thus the molecule of  $\beta$ -stannic acid appears to contain five tin atoms, and the air-dried acid becomes  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 9\text{H}_2\text{O}$  instead of  $\text{SnO}_2 \cdot 21\text{H}_2\text{O}$ , whilst the acid dried in a vacuum is  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 11\text{H}_2\text{O}$  instead of simply  $\text{SnO}_2 \cdot \text{H}_2\text{O}$ . Alternative formulae are  $\text{Sn}_5\text{O}_7(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$  and  $\text{Sn}_5\text{O}_7(\text{OH})_{10}$  respectively, which suggest that  $\beta$ -stannic acid may possibly contain a ten-membered ring of alternated tin and oxygen atoms. At least an analogy is suggested between  $\beta$ -stannic acid and the polymerised silicic acids.

$\beta$ -stannic acid is distinguished from the  $\alpha$ -acid by its insolubility in dilute nitric and sulphuric acids. It does not dissolve in cold con-

<sup>1</sup> Boyle, *Opuscula*, 1670, 4, 281.

<sup>2</sup> Boyle, *Experiments and Considerations concerning Colours*, 1664.

<sup>3</sup> Kunkel, *Laboratorium Chymicum*, 1716.

<sup>4</sup> Lorenz, *Zeitsch. anorg. Chem.*, 1895, 9, 376.

<sup>5</sup> Graham, *Phil. Trans.*, 1861, 151, 213.



concentrated sulphuric acid, but with the hot acid forms stannic sulphate, which by hydrolysis yields  $\alpha$ -stannic acid. Hydrochloric acid dissolves the  $\beta$ -acid, but excess of it precipitates  $\beta$ -stannyl chloride (*q.v.*), which was formed in solution. The  $\beta$ -acid may be converted into a salt of the  $\alpha$ -acid by fusion with potash or by long-continued boiling with concentrated potash solution. Evaporation to dryness with hydrochloric acid also yields the  $\alpha$ -acid.

**Parastannic Acid.**—It was found by Berzelius that when  $\beta$ -stannic acid is heated with water at  $100^{\circ}\text{C}$ . it passes into another form of stannic acid, which when air-dried has the empirical composition  $5\text{SnO}_2 \cdot 8\text{H}_2\text{O}$ , and is probably  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 7\text{H}_2\text{O}$ . This compound when dried in a vacuum becomes  $5\text{SnO}_2 \cdot 3\text{H}_2\text{O}$  or  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot 2\text{H}_2\text{O}$ , rather than  $\text{SnO}_2 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{Sn}_5\text{O}_{11} \cdot \text{H}_2\text{O}$ , which is  $\beta$ -stannic acid. The potassium salt of parastannic acid is  $\text{K}_2\text{Sn}_5\text{O}_{11} \cdot 2$  or  $3\text{H}_2\text{O}$ , to which parastannyl chloride, shortly to be described, corresponds.

**$\beta$ -Stannyl Chloride**,  $\text{Sn}_5\text{O}_9\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ , is related to  $\beta$ -stannic acid, which may be written  $\text{Sn}_5\text{O}_9(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; and it may, therefore, be regarded as the chloride of this acid. An alternative view is to consider the hydroxide as amphoteric, and as behaving as a diacid base, of which  $\beta$ -stannyl chloride is a salt. Because of the mode of formation and properties of the chloride this latter view is perhaps to be preferred; thus it is a basic stannic chloride.

$\beta$ -stannyl chloride is prepared by first acting on tin with nitric acid of density 1.3 to 1.4, the temperature being kept low to prevent the formation of parastannic acid; hydrochloric acid is then added to the resulting  $\beta$ -stannic acid, and the gelatinous mass produced is diluted with water and filtered. The filtrate is precipitated with hydrochloric acid, the precipitate washed with the acid diluted with an equal volume of water, and the product dried in a vacuum over sulphuric acid and potash. The  $\beta$ -stannyl chloride thus obtained is a transparent, glassy mass which contains nine or four molecules of water to one molecule of  $\text{Sn}_5\text{O}_9\text{Cl}_2$ , according to whether it has been dried in air or in a vacuum. It is soluble in dilute hydrochloric acid, and unlike stannic chloride is reprecipitated by the strong acid. This compound is also formed by hydrolysis when dilute solutions of stannic chloride are kept.

**Parastannyl Chloride**,  $\text{Sn}_5\text{O}_9\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , is produced by acting on parastannic acid with concentrated hydrochloric acid, dissolving the product in water, and precipitating the opalescent solution thus produced with more acid; the precipitate is then dried in a vacuum. This chloride is also formed in solution when a hydrochloric acid solution of  $\beta$ -stannyl chloride is warmed.

## TIN AND SULPHUR

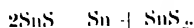
### TIN SULPHIDES

**Stannous Sulphide**,  $\text{SnS}$ , is formed in the dry way when tin-foil is heated with sulphur<sup>1</sup>; the metal, indeed, takes fire spontaneously when brought into sulphur vapour. This sulphide may be sublimed in a current of hydrogen, and forms a shining crystalline mass, resembling graphite. Glistening, metallic scales are also formed when the sulphide

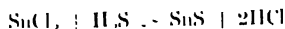
<sup>1</sup> Ditte, *Compt. rend.*, 1883, 96, 1790.

## TIN AND ITS COMPOUNDS

is heated in the electric furnace.<sup>1</sup> Stannous sulphide melts at 881° C., and boils at 1090° C., producing a green vapour; and when heated to 265° C. under pressure it decomposes into tin and stannic sulphide, thus:



Stannous sulphide is precipitated in a brown, hydrated form when a slightly acidified solution of stannous chloride is saturated with hydrogen sulphide gas; on drying, the precipitate turns black. The solubility of this precipitate in acids and alkalis is instructive. Thus it readily dissolves even in somewhat diluted hydrochloric acid, and consequently is imperfectly precipitated if much acid is present, the reaction

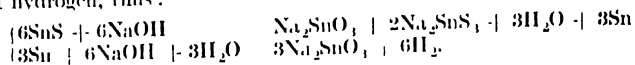


being a reversible one which proceeds to an equilibrium.<sup>2</sup>

This solubility may be referred to the base-producing properties of tin; and consequently, as might be inferred, stannous sulphide is indifferently soluble in alkali solutions, though its solubility varies with its physical state.<sup>3</sup> The freshly precipitated sulphide dissolves slowly on boiling with dilute caustic soda solution, producing a mixture of stannite and thio-stannite. Since the former salt is  $\text{HSnOONa}$ , the latter is probably constituted similarly, so that the reaction is:



The sulphide is reprecipitated from this solution by acid. Strong alkalis may, however, decompose stannous sulphide into stannic sulphide and tin, the former of which dissolves, forming thio-stannate, whilst the latter reacts with the alkali, producing stannate with evolution of hydrogen, thus:



**Stannic Sulphide**,  $\text{SnS}_2$ , has long been known and valued as a pigment. It is prepared for this purpose by heating together 12 parts of tin, 6 parts of mercury, with which the tin forms an amalgam, 7 parts of sulphur, and 6 parts of sal ammoniac. Stannous chloride, mercuric chloride, and the remaining sal ammoniac sublime, and golden-yellow scales of stannic sulphide remain. It may also be obtained by heating stannous sulphide with corrosive sublimate, and in other ways.<sup>4</sup> The product crystallises in hexagonal tablets, which are translucent and of a golden colour. It has, therefore, been known since the eighteenth century as *mosaic gold*, *aurum mosaicum* or *mosaion*. The density of this substance is about 4.5, and it is employed as a bronzing powder for articles of wood, gypsum, etc. When it is heated sufficiently it is partly decomposed into stannous sulphide and sulphur, whilst the rest sublimes. It dissolves in aqua regia and in caustic alkali, but not in hydrochloric or nitric acid. Stannic sulphide is met with in analysis as a dull

<sup>1</sup> Biltz and Mecklenberg, *Zetsch. anorg. Chem.*, 1909, 64, 226.

<sup>2</sup> Moutlot, *Compt. rend.*, 1897, 124, 768.

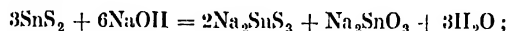
<sup>3</sup> Ditté, *Compt. rend.*, 1883, 97, 112.

<sup>4</sup> F. M. Perkin, *J. Soc. Chem. Ind.*, 1901, 20, 125.

<sup>5</sup> Woulfe, *Phil. Trans.*, 1771, 114. Klotzinsky, *Dingl. polyt. J.*, 1864, 174, 245; Pelletier, *Ann. Chim. Phys.*, 1792, [v], 13, 280; Schneider, *Pogg. Annalen*, 1855, 95, 169.

**yellow** formed when hydrogen sulphide gas is passed into a solution. According to Jorgensen,<sup>1</sup> the precipitate is a mixture of stannous sulphide and a hydrochloric solution of metastannic acid and stannic acid in variable amounts of metastannic acid and stannic acid depending on the concentration of the acid and the temperature and the time. Although the precipitate contains little stannic sulphide at first it is gradually transformed into this substance in contact with hydrogen sulphide solution, though the process requires about two months for completion.

Precipitated stannic sulphide dissolves in concentrated hydrochloric acid, though less readily than stannous sulphide. It dissolves easily in caustic alkali solutions, forming a mixture of thiostannate and stannate, thus :



and in alkali sulphide solutions forming thiostannate only. Stannous sulphide may also be converted into thiostannate, and so more easily dissolved, by heating it with alkali polysulphide solution or with alkali hydroxide and flowers of sulphur.

**Thiostannic Acid and its Salts.** When a solution of precipitated stannic sulphide in alkali sulphide is reprecipitated with acid a yellowish brown solid separates, which on drying becomes almost black. This is thiostannic acid,  $\text{H}_2\text{SnS}_3$ , which on heating, in absence of air, loses hydrogen sulphide, yielding the yellow disulphide.<sup>2</sup> Potassium thiostannate is obtained in colourless prisms, having the composition  $\text{K}_2\text{SnS}_3 \cdot 3\text{H}_2\text{O}$ , from its solution formed by boiling concentrated potassium sulphide solution with tin and sulphur. The sodium salt,  $\text{Na}_2\text{SnS}_3 \cdot 2\text{H}_2\text{O}$ , is formed similarly ; whilst by fusing together sodium sulphide, stannous sulphide and sulphur, extracting the mass with water, and concentrating the solution, colourless crystals of the ortho-salt,  $\text{Na}_2\text{SnS}_4 \cdot 12\text{H}_2\text{O}$ , are obtained. The ammonium salt  $(\text{NH}_4)_2\text{SnS}_3 \cdot 3\text{H}_2\text{O}$  is obtained in unstable yellowish tablets by precipitating a solution of stannic sulphide in yellow ammonium sulphide by alcohol.<sup>3</sup>

**Stannic Oxysulphide**,  $\text{Sn}_2\text{OS} \cdot 11\text{H}_2\text{O}$ , is obtained as a white solid, which gradually turns yellow on keeping, by precipitating an ammoniacal solution of stannic sulphide with acid.<sup>4</sup>

**Stannic Iodosulphide**,  $\text{SnS}_2\text{I}_2$ , is said to be formed when stannic sulphide and iodine, in the theoretical proportions, are fused together in a stream of carbon dioxide.<sup>5</sup> The product sublimes in yellowish red crystals, which are soluble in chloroform and carbon disulphide ; but water decomposes the compound into stannic oxide, hydriodic acid, and sulphur.

#### TIN SULPHATES

**Stannous Sulphate**,  $\text{SnSO}_4$ , is obtained when the metal or hydrated monoxide is dissolved in dilute sulphuric acid, or when the former is digested with a mixture of one volume of sulphuric acid, two of nitric

<sup>1</sup> Jorgensen, *Zeitsch. anorg. Chem.*, 1901, 28, 110.

<sup>2</sup> Kuhn, *Annalen*, 1852, 84, 110.

<sup>3</sup> Stanek, *Zeitsch. anorg. Chem.*, 1898, 17, 117.

<sup>4</sup> Schmidt, *Ber.*, 1894, 27, 2739.

<sup>5</sup> Schneider, *J. prakt. Chem.*, 1860, 79, 419.

acid, and three of water.<sup>1</sup> The salt is obtained in white, anhydrous needles on evaporating its solution in a vacuum; 18.8 grams of stannous sulphate dissolve in 100 grams of water at 19° C., and 18.1 grams at 100° C.; its solution is easily hydrolysed with the deposition of a basic salt. The anhydrous salt when heated above 360° C. evolves sulphur dioxide by self-oxidation and reduction, thus:<sup>2</sup>



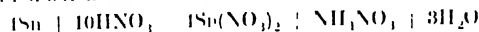
**Stannic Sulphate.**--The feebly basic properties of stannic oxide do not admit of the formation of a stable sulphate; and this is shown by the precipitation of stannic hydroxide when sodium sulphate is added to stannic chloride solution. Nevertheless a crystalline salt of the composition  $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  is obtained when freshly precipitated stannic hydroxide is dissolved in dilute sulphuric acid and the solution is evaporated.<sup>3</sup> The same salt may be obtained from the solution of stannic oxide in concentrated sulphuric acid, and also a basic salt of the composition  $\text{Sn}(\text{SO}_4)_2 \cdot \text{SnO}_2 \cdot 2\text{H}_2\text{O}$ . Both salts are completely hydrolysed by water.

#### TIN AND SELENIUM AND TELLURIUM

Tin forms a compound with selenium of the composition  $\text{SnSe}$ , which melts at 861° C., and another, which is either  $\text{Sn}_2\text{Se}_3$  or  $\text{SnSe}_2$ , which melts near 650° C. These facts have been established by the study of freezing-point curves of mixtures of the two elements, and the similar study of tin-tellurium mixtures shows the existence of the compound  $\text{SnTe}$  corresponding with a well-marked maximum at 800° C. Microscopic examination shows that the compounds  $\text{SnSe}$  and  $\text{SnTe}$  crystallise well.<sup>4</sup>

#### TIN AND NITROGEN

**Stannous Nitrate** is obtained in white tablets having the composition  $\text{Sn}(\text{NO}_3)_2 \cdot 20\text{H}_2\text{O}$  by cooling to -20° C. a solution of stannous oxide in nitric acid of density 1.2. It is also formed by the action of highly diluted nitric acid on the metal, some of the acid thus suffering maximum reduction to ammonia:



According to C. H. H. Walker,<sup>5</sup> tin dissolves in nitric acid forming stannous and stannic nitrates, the relative proportion of these two salts produced depending on the temperature and the strength of the acid; moreover, the yellowish white precipitate which separates when the somewhat concentrated acid is employed is said to be a hydrated, ill-defined, stannic nitrate.

**Stannic Nitrate**,  $\text{Sn}(\text{NO}_3)_4$  is said to be produced by the action of 70 per cent. nitric acid on tin, and to be stable in presence of the concentrated acid at 90° C.<sup>6</sup> It dissolves in water but is quickly hydrolysed with separation of hydrated stannic oxide.

<sup>1</sup> Basset *Chem. News*, 1886, 53, 172.

<sup>2</sup> Durant, *Trans. Chem. Soc.*, 1915, 107, 630.

<sup>3</sup> Ditté *Compt. rend.*, 1887, 104, 172.

<sup>4</sup> Biltz, Mecklenberg and Goldbeck, *Zeitsch. anorg. Chem.*, 1909, 64, 226.

<sup>5</sup> Walker *Trans. Chem. Soc.*, 1893, 63, 845.

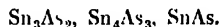
<sup>6</sup> Montemartini, *Gazzetta*, 1892, 22, 381.

## TIN AND PHOSPHORUS AND ARSENIC

**Phosphor-tin**, made by adding phosphorus to molten tin, is largely employed in the preparation of phosphor-bronze. It is characterised by extreme brittleness and brilliant fracture; and microscopic examination of its surface shows it to be traversed by numerous intercepting straight lines, between which is a softer matrix. By treatment of the alloy with dilute nitric acid the matrix is removed, and a **phosphide of tin** in the form of white, shining plates remains, which is found to have the composition  $\text{Sn}_3\text{P}_2$ .<sup>1</sup> When this compound is heated in hydrogen some of the phosphorus is removed, and when it is acted upon by concentrated hydrochloric acid spontaneously inflammable phosphine is liberated. If the phosphide  $\text{Sn}_3\text{P}_2$  is heated alone it loses some phosphorus, yielding a lower phosphide of the composition  $\text{Sn}_2\text{P}$ , which may also be obtained by the union of phosphorus with spongy tin. When, however, finely divided tin is heated in phosphorus vapour, the compound  $\text{SnP}$  is obtained as a white, brittle mass.

**Stannic Phosphate or Pyrophosphate** is a solid of rather indefinite composition formed by the combination of phosphoric and  $\beta$ -stannic acids. The formation of this substance serves to separate phosphoric acid from a nitric acid solution, and is sometimes employed for this purpose in qualitative analysis. Tin-foil is added to the nitric acid solution of a mixture containing phosphate, and all the phosphoric acid enters into combination with the  $\beta$ -stannic acid as it is formed, so that the solution is freed from phosphate.<sup>2</sup>

There is metallographic evidence of the existence of the following **arsenides of tin** <sup>3</sup>:



## TIN AND CARBON

**Stannioxalic Acid.**—It was shown by Hansemann and Lowenthal<sup>4</sup> that freshly precipitated stannic hydroxide is freely soluble in oxalic acid solution, and that when this solution is evaporated a gummy mass remains; and Péchard,<sup>5</sup> by dissolving stannic hydroxide in potassium hydrogen oxalate solution obtained monoclinic crystals, to which he attributed the formula  $\text{K}_2\text{O} \cdot \text{SnO}_2 \cdot 2\text{C}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ . Rosenheim and Platsch<sup>6</sup> isolated, however, in the same way, crystals having the composition  $3\text{K}_2\text{O} \cdot 2\text{SnO}_2 \cdot 7\text{C}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , and showed that a solution of this substance gives the reactions neither of tin nor of oxalic acid. It is, therefore, the potassium salt of a complex stannioxalic acid. The barium salt,  $2\text{BaO} \cdot \text{SnO}_2 \cdot 4\text{C}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , obtained by adding barium chloride to a solution of the potassium salt, forms insoluble white needles. The free acid could not be obtained; attempts to isolate it

<sup>1</sup> Stead, *J. Soc. Chem. Ind.*, 1897, 16, 200

<sup>2</sup> Mecklenberg, *Zeitsch. anal. Chem.*, 1913, 58, 293

<sup>3</sup> Jobbins and Dupuy, *Compt. rend.*, 1911, 152, 1312; Pattavano and de Cesaris, *Atti Accad. Lincei*, 1911, [v], 20, 1, 593.

<sup>4</sup> Hansemann and Lowenthal, *Annalen*, 1851, 89, 104

<sup>5</sup> Péchard, *Compt. rend.*, 1893, 116, 1513

<sup>6</sup> Rosenheim and Platsch, *Zeitsch. anorg. Chem.*, 1899, 20, 281

## TIN AND ITS COMPOUNDS

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yielded mixtures of colloidal stannic acid and oxalic acid. This power of stannic tin to combine with oxalic acid furnishes a means for the analytical separation of the metal.

**Stannous Tartrate**,  $\text{SnC}_4\text{H}_4\text{O}_6$ , is slowly formed when a dilute solution of tartaric acid acts upon tin in presence of air.<sup>1</sup>

## TIN AND SILICON AND TUNGSTEN

**Tin and Silicon.** Liquid silicon and tin mix in all proportions, and, on cooling, pure silicon separates, the eutectic being practically pure tin.<sup>2</sup>

**Stannous Tungstate**,  $\text{SnWO}_4 \cdot 6\text{H}_2\text{O}$ , is formed as a yellow precipitate when solutions of stannous chloride and potassium tungstate are mixed. It is soluble in oxalic acid and potassium hydroxide solutions.

## DETECTION AND ESTIMATION OF TIN

**Detection and Qualitative Separation.** Tin is tested for qualitatively by reactions in the dry way and in solution.

Tin compounds are reduced to the metal when heated on a carbonised match in the inner blowpipe flame, or when mixed with potassium cyanide and heated on charcoal before the blowpipe. The bead of metal thus obtained is white and malleable, but quickly becomes covered, when hot, with a film of white oxide. The metal may be identified by its behaviour with nitric acid, by fusing a particle of it into a borax bead coloured blue with a copper salt, when the bead becomes ruby-red, or by dissolving it in hydrochloric acid and adding mercuric chloride to the solution of stannous chloride thus formed, when a white precipitate of mercurous chloride, or a grey one of mercury, will be obtained. Tin compounds colour the Bunsen flame greyish blue, but give no spectrum in this way.

Stannous and stannic compounds are capable of numerous reactions in solution, which have been given in detail in the previous pages; therefore only those of analytical importance will here be noticed.

If a tin compound cannot be dissolved in hydrochloric acid, as, for instance, stannic oxide, it may be fused with sodium or potassium hydroxide, or, better, with a mixture of sodium carbonate and sulphur, which produces sodium stannate. After the excess of sulphur has been vapourised there remains a dark brown mass which will dissolve completely in water, yielding a yellow solution. From this solution dilute hydrochloric acid precipitates stannous acid,  $\text{H}_2\text{SnS}_3$ , which may then be dissolved in concentrated hydrochloric acid.

Stannous and stannic sulphides are precipitated from slightly acid solution by hydrogen sulphide, and so are brought down with the other metals of the second analytical group. Stannous sulphide, however, is rather easily dissolved by hydrochloric acid; and, therefore, unless the solution is well diluted, will be incompletely precipitated. Both sulphides, together with those of arsenic and antimony, are separated from the other sulphides of the group by reason of their solubility in alkali solutions. Stannous sulphide is, however, imperfectly dissolved

<sup>1</sup> Chapman *Trans. Chem. Soc.*, 1913, 103, 775

<sup>2</sup> Tamura, *Zeitsch. anorg. Chem.*, 1909, 61, 40

by sodium hydroxide solution ; but dissolves more readily in presence of a polysulphide, such as may be formed by heating the alkali solution with sulphur, or adding to it yellow ammonium sulphide. This is because stannous is thereby converted into stannic sulphide, which produces thio-stannate.

If arsenic and antimony were originally present with tin their sulphides will all be present in the alkaline solution as thio-salts, whence they will be precipitated together by dilute acid. Various means are available for the separation and identification of these three metals. Arsenic may be separated from antimony and tin by either of two methods :

(i) Boiling concentrated hydrochloric acid dissolves the sulphides of antimony and tin, but has no action on sulphide of arsenic.

(ii) Digestion with water and solid ammonium carbonate dissolves sulphide of arsenic, but not the sulphides of antimony and tin, which may be dissolved in hydrochloric acid after the removal of the arsenic.

The following methods are available for separating antimony and tin present in hydrochloric acid solution :

(i) The acid solution is poured upon a piece of zinc resting on platinum foil in a dish ; when by electrolytic action metallic antimony is deposited on the platinum, and tin upon the zinc. The deposited tin may then be dissolved in concentrated hydrochloric acid, and tested for, after diluting the solution, by means of mercuric chloride.

(ii) Antimony may be removed and tin left in solution by passing hydrogen sulphide gas after addition of oxalic acid, since the stannic-oxalic acid thus formed contains no tin ions to be precipitated by hydrogen sulphide. Tin may then be precipitated from the filtrate from the antimony sulphide by metallic zinc, or the oxalic acid may be destroyed by permanganate, and the tin then precipitated by hydrogen sulphide.

(iii) Sodium hydroxide is added to the solution containing tin and antimony until the precipitated hydroxides are redissolved ; bromine water is then added to convert stannite and antimonite into stannate and antimonate, and this is followed by solid ammonium chloride. After the evolution of nitrogen by the action of hypobromite on ammonia, a precipitate of stannic hydroxide separates owing to the hydrolysis of ammonium stannate ; and this, after boiling the liquid, may be filtered off, leaving antimonate in solution. The stannic hydroxide is then dissolved in hydrochloric acid, the solution reduced to the stannous state by iron wire, and the tin tested for by mercuric chloride.<sup>1</sup>

(iv) Another method of detecting antimony and tin, which is very simple and satisfactory, consists in causing iron wire to react with the hydrochloric acid solution of the mixed chlorides. By this means metallic antimony is separated as a black powder, and tin is reduced to the stannous state, and may be detected, after the solution has been filtered, by the mercuric chloride test.

**Estimation.**—Tin may be estimated : (a) volumetrically, (b) gravimetrically, (c) electrolytically.

(a) Tin when present in the stannous state is estimated volumetrically by titration with standard iodine solution. It is usual to add Rochelle salt to the solution, and then excess of sodium bicarbonate. The latter combines with the hydriodic acid formed so as to prevent

<sup>1</sup> Walkor, *Trans. Chem. Soc.*, 1903, 83, 181 ; Caven, *Proc. Chem. Soc.*, 1910, 26, 176

the reversal of the reaction, and the Rochelle salt serves to retain the tin in solution as a complex tartrate. The results are apt to be low owing to atmospheric oxidation of the stannous salt, and it is, therefore, preferable at once to add excess of iodine and titrate back with thio-sulphate. Tin may be estimated in acid solution by adding iodine in excess, and titrating back with dilute stannous solution of known strength, and also by adding excess of ferric chloride which converts stannous into stannic chloride, and titrating with dichromate the ferrous iron produced. When tin is present in solution in the stannous state, the metal may be precipitated by zinc, then dissolved in hydrochloric acid, and the solution titrated with iodine.

(b) Tin is estimated gravimetrically as dioxide, into which the metal is converted by the action upon it of nitric acid, followed by the ignition of the  $\beta$ -stannic acid so formed. When the tin is present in an alloy, the stannic oxide so obtained will not be pure. If copper and iron are present they may be separated by fusing the impure stannic oxide with sodium carbonate and sulphur, dissolving the fused mass in water, and reducing the solution with sodium sulphite, when the sulphides of iron and copper will be precipitated and may be filtered off and weighed. Instead of weighing the iron and copper sulphides it is permissible to reprecipitate the stannic sulphide from the filtrate, convert it into stannic oxide by ignition and weigh it as such. When the alloy contains antimony, this metal will be present as a thio-salt together with tin after fusion of the oxides of these metals with sodium carbonate and sulphur. The solution containing the mixed thio-salts is treated with caustic potash, hydrogen peroxide, and tartaric acid<sup>1</sup> to convert thio- into oxy-salts and retain the latter in solution. Oxalic acid is then added, followed by hydrogen sulphide. By this means tin is kept in solution, whilst the antimony is precipitated as the pentasulphide.<sup>2</sup> It is then usual to estimate the tin in the filtrate electrolytically.

(c) Tin when present in solution as stannous chloride, may be estimated electrolytically by the method of Engels,<sup>3</sup> by adding to the solution hydroxylamine to prevent oxidation, together with tartaric acid and ammonium oxalate, and passing a current of electricity through the warm solution. It is difficult, however, to remove all the tin.

Classen<sup>4</sup> separates antimony electrolytically from a solution of the sulphides in concentrated sodium sulphide, tin not coming down if the current is weak.

Sand<sup>5</sup> has carried out the rapid electrolytic estimation of tin, and its separation from antimony. The pure metal was dissolved in concentrated sulphuric acid, and the solution was diluted and nearly neutralised by ammonia, oxalic acid being added to keep the stannous tin in solution. From this solution, by the use of rotating platinum electrodes, about 0.3 gram of tin was completely separated in thirty minutes or less at a temperature of 70°–100° C., with a current of 3 to 5 amperes and 2 to 4 volts. If the solution was old, and therefore contained some  $\beta$ -stannic compound, the separation was more difficult.

<sup>1</sup> Heuz, *Annales Des chimies*, Zurich, 1903.

<sup>2</sup> See also McCay, *J. Amer. Chem. Soc.*, 1910, 32, 1241.

<sup>3</sup> Engels, *Zeitsch. Elektrochem.*, 1896, 2, 418.

<sup>4</sup> Classen, *Ber.*, 1884, 17, 2245; 1885, 18, 1110; 1895, 28, 2000.

<sup>5</sup> Sand, *Trans. Chem. Soc.*, 1908, 93, 1572, see also Pasztor, *Zeitsch. Elektrochem.*, 1910, 16, 281.



The separation of antimony from tin in an alloy such as type-metal has been carried out successfully by the use of a graded potential. The alloy was dissolved in a mixture of nitric and sulphuric acids; the greater part of the nitric acid was expelled by heating, and the remainder destroyed; and then the antimony was reduced to the antimonious state by hydrazine sulphate. Finally, the antimony was separated at a limited potential from the sulphuric acid solution, leaving the tin behind.

Tin may also be estimated<sup>1</sup> electrolytically after precipitation as sulphide by dissolving the precipitate in ammonium sulphide solution, adding sodium sulphate, and electrolysing the solution.

The electrochemical behaviour of tin has been studied by Foerster and Yamasaki<sup>2</sup>

<sup>1</sup> Humphreys *Anal. and Mag. J.*, 1914, 98, 964, *J. Soc. Chem. Ind.*, 1914, 33, 1228

<sup>2</sup> Foerster and Yamasaki, *Zeitsch. Elektrochem.*, 1911, 17, 361

## CHAPTER IX

### LEAD AND ITS COMPOUNDS

#### LEAD

Symbol, Pb    Atomic weight, 207.20 (O    16)

**Occurrence.** Lead rarely occurs native. Its most important ore is the sulphide, *galena*,  $\text{PbS}$ , with which are occasionally associated the selenide and telluride. The common occurrence of galena is to be attributed to its relative insolubility in water, the readiness with which it crystallises, and the fact that it is formed from other compounds by various reactions, both wet and dry. Probably its natural formation is commonly due to the action of hydrogen sulphide on other lead compounds in presence of water. It is found associated with quartz, fluorapat, calcapat, and barites in various geological strata, is widely distributed throughout the world, and occurs in veins or flat beds between the strata. In Cornwall and Devon, galena lies in veins called "kylas" within an argillaceous schist of the Devonian formation; in and around Alston Moor, at the junction of Northumberland, Cumberland, and Durham, the same ore is found in flat veins or "flats" in carboniferous limestone; in Shropshire, parts of Wales and Scotland, and the Isle of Man, the ore occurs in rocks of the Silurian formation; whilst in parts of Ireland it is found in granite.

Though of little practical importance, the complex sulphides in which lead is associated with other metals are numerous and interesting, and include thioarsenides, thioantimonides, thioarsenitides, and thioantimonides. Typical minerals of this kind are *santonite*,  $\text{PbAs}_2\text{S}_4$ ; *zinkenite*,  $\text{PbSb}_2\text{S}_4$ ; *bournonite*,  $\text{CuPbSbS}_4$ . Zinkenite has been produced artificially by fusing together galena and stibnite in the proper proportions.<sup>1</sup> If the sulphide is regarded as the fundamental lead mineral other minerals are derived from it by oxidation, carbonation, etc. The oxides are rarely found, but occur as *massicot*,  $\text{PbO}$ ; *minum*,  $\text{Pb}_2\text{O}_3$ ; and *plattnerite*,  $\text{PbO}_2$ .

*Cerussite*, lead carbonate,  $\text{PbCO}_3$ , ranks next in importance to galena as a lead ore. Its formation is attributed to the action of carbonated waters on other lead compounds. It is found in Devon and Cornwall, in Yorkshire, at Leadhills in Scotland, and in County Wicklow. A basic carbonate, known as *hydrocerussite*, is  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ .

Lead chloride,  $\text{PbCl}_2$ , occurs as the rare mineral *colunite*, produced as a sublimate in volcanic action; the basic chlorides, *matlockite*,  $\text{Pb}_2\text{OCl}_2$ , and *mendipite*,  $\text{Pb}_3\text{O}_2\text{Cl}_2$ , are better known, but the chlorocarbonate, *phosgenite*,  $\text{Pb}_2\text{Cl}_2\text{CO}_3$ , is rare.

*Anglesite*, lead sulphate,  $\text{PbSO}_4$ , is a mineral of some importance, occurring at Leadhills and elsewhere; it may have been formed as an oxidation product of galena, or by the action upon this mineral

<sup>1</sup> Fournet, *J. prakt. Chem.*, 1834, 2, 490.

of acid ferrous sulphate solutions formed by the oxidation of pyrites. Basic lead sulphate,  $\text{Pb}_2\text{SO}_4$ , occurs as the rare mineral *lanarkite*, whilst *leadhillite* is  $\text{PbSO}_4 \cdot 2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ .

Lead chromate,  $\text{PbCrO}_4$ , occurs as *crocoite* or *crocosite*, the molybdate  $\text{PbMoO}_4$ , as *wulfenite*, the tungstate  $\text{PbWO}_4$ , as *stolzite*.

Lastly there are three minerals which are interesting on account of their isomorphism: the chlorophosphate *pyromorphite*  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ , the chloroarsenate *minette* or *minetesite*  $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ , and the chlorovanadate *vanadinite*  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ .

**History.**—Lead was one of the seven metals known to the ancients; and the Egyptians were probably acquainted with it three thousand years ago. It is mentioned several times in the Old Testament; and, together with tin, was found amongst the spoil taken by Israel from the Midianites (Numbers xxxi, 22). The name used for it was *ôphéret*, derived from *âphâr*, signifying grey. The Greek equivalent of this word is *μολύβδος*, to which is related the word *μολύβδος*, which originally meant lead. It is doubtful how far lead was distinguished from tin in the earliest times; a distinction was drawn, however, by Pliny between these two metals; for, according to him, lead was *plumbum nigrum*, whilst tin was *plumbum album* or *candidum*. Lead, or an alloy containing it, appears to have been used by the Romans for pipes for conveying water.

According to their custom of associating metals with the heavenly bodies the alchemists apportioned lead to Saturn, and gave it the symbol  $\text{♄}$ . Thence arose the adjective *saturnine*, which meant pertaining to lead; e.g. *minium* was known as *saturnine red*. It is interesting to notice that this adjective is still employed to signify the lead-like qualities of dullness and heaviness.

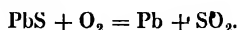
#### THE METALLURGY OF LEAD<sup>1</sup>

Owing to its easy reducibility lead was extracted from its ores in very early times. The Romans manufactured lead in Britain, and the remains of rough furnaces exist in Derbyshire and elsewhere, in which the ore was reduced by means of charcoal. Until the middle of the eighteenth century a kind of blast-furnace was in use in England, but about this time reverberatory furnaces, previously employed in Flintshire, were introduced into this country.

Three distinct processes are now employed in the metallurgy of lead:

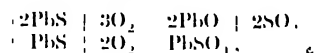
- (i) The air reduction process.
- (ii) The carbon reduction process.
- (iii) The precipitation process.

(i) **The Air Reduction Process** is applicable to ores consisting chiefly of galena, and free from other metallic sulphides and silica. The term "air reduction" seems anomalous. It applies to the preferential oxidation of sulphur, whereby from galena, metallic lead and sulphur dioxide result thus:

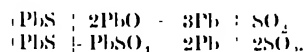


<sup>1</sup> For a detailed account of the practical Metallurgy of Lead, see *Lead*, by H. F. Collins, 2nd edn. (C. Griffin and Co., Ltd., 1910).

This reaction is not, however, directly realised; but the following reactions of oxidation first take place:

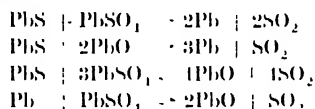


and these are followed by the interaction of unchanged lead sulphide with oxide and sulphate thus:

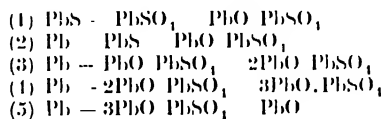


The latter reaction, however, is liable to be reversed by the action of excess of sulphur dioxide on the reduced lead.

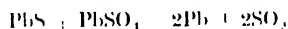
Four conditions of equilibrium, indeed, are possible, and are represented by the equations<sup>1</sup>



According to Remdes,<sup>2</sup> in the interaction of lead sulphide with lead sulphate, and the formation of metallic lead and sulphur dioxide, the five following univalent systems, each consisting of three solid phases, successively occur and mark the gradual diminution of sulphur:



From the vapour pressure curve of the first system the thermal value of the reaction



is calculated to be -99,543 calories; and from the heats of formation of the compounds concerned to be -92,470 calories at 20° C.

These reactions are carried out in a reverberatory furnace (Fig. 13).

The charge of ore, consisting of from 12 to 21 cwt., is introduced through the hopper on to the hearth of the furnace, which is hollowed so as to allow the molten lead to collect above the tapping hole, and flow through it at the proper time into an iron pot. There are several doors surrounding the hearth which allow the temperature to be regulated and the mass to be rabbled at intervals.

In the first part of the operation the ore is heated below a full red heat, and not allowed to clot, and thus absorption of oxygen takes place with the formation of oxide and sulphate according to the first two reactions. When this oxidation is at an end the doors of the furnace are closed, and the temperature is raised to a full red heat, and thus maintained for about half an hour. The mass now becomes plastic, reduction to metallic lead takes place, and the molten metal

<sup>1</sup> Jenkins and Smith, *Proc. Chem. Soc.*, 1897, 13, 404; Schneck and Rassbach, *Ber.*, 1907, 40, 2185, 2947.

<sup>2</sup> Remdes (with Goudriaan), *Proc. Koninkl. Akad. Wetensch. Amsterdam*, 1914, 17, 703.

collects in the well of the furnace. In order, however, to separate the metal from unreduced ore, the furnace is allowed to cool somewhat, and lime is added and mixed with the charge by means of a rake. This makes a stiff slag, from which the molten metal more easily separates, and also serves to combine with any silica present, and liberate lead oxide with which the silica may have been combined. Lastly, the temperature is again raised, and more lime is added, so as further to stiffen the slag; then the molten metal is run off from the taphole, and the solid slag, technically known as *grey slag*, raked out from the furnace. Some slag, however, still remains with the metal, and this is eliminated by stirring coal slack into the mass by

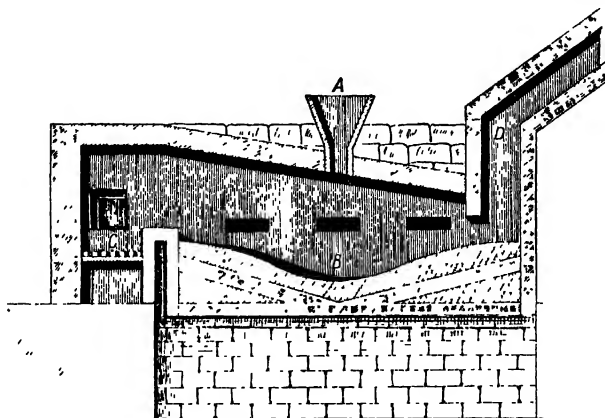


FIG. 13. Flintshire reverberatory furnace for lead smelting.

- |                           |                 |
|---------------------------|-----------------|
| A Hopper                  | C Furnace place |
| B Hollowed bed of furnace | D Flue          |

means of a paddle. The combustion of the coal melts and liberates the metal confined in the slag, and the latter is then skimmed off from the surface of the metal.

The slag may contain as much as 40 per cent. of lead, which is recovered by treatment in a special blast-furnace called a slag-hearth, or in the blast-furnace employed in method (ii). Ores smelted by the air reduction process in Flintshire contain from 75 to 80 per cent. of lead, 90 per cent. of which is obtained directly from the reverberatory furnace, and the remainder by the subsequent treatment of the slag.

(ii) **The Carbon Reduction Process.**—Ores in which lead exists as oxide or carbonate can readily be reduced by carbon, after the manner in which iron ores are reduced in the blast-furnace. Moreover, lead sulphide, occurring as galena, may be converted into oxide by efficient roasting, and this oxide may subsequently be reduced in the same way. Besides this, the method of carbon reduction in a blast-furnace is applicable to ores containing silica, iron and copper pyrites, and other minerals. Consequently, the carbon reduction process is now perhaps the most important part of the metallurgy of lead.

The blast-furnace (Fig. 14) in which lead ores are smelted is rectangular, and about 3 feet 6 inches wide, and 12 feet high above the tuyères. The lower part or bosh of the furnace is made of cast-iron or steel, and surrounded by a water-jacket through which the tuyères pass; the rest of the furnace is lined with fire-brick.

The preliminary process of roasting is carried out in a reverberatory furnace, or in a vessel shaped like a Bessemer converter, through which air is blown. When the lead sulphide has been converted into oxide

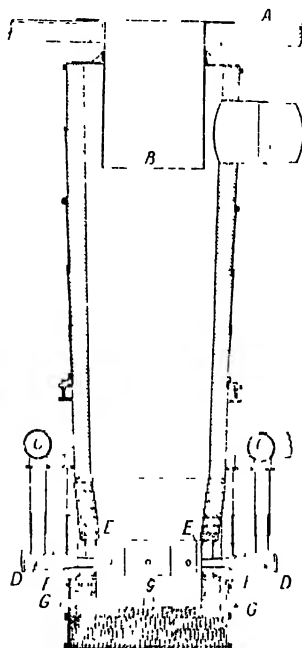


FIG. 14. Blast-furnace for lead smelting.

- |                            |                             |
|----------------------------|-----------------------------|
| A. Churn in roof           | I. Water-jacket surrounding |
| B. Churner pipe            | bottom of furnace           |
| C. Blast main              | F. Storage                  |
| D. Tuyères, or blast-pipes | G. Tapholes                 |

and sulphate, the roasted ore is heated to incipient fusion which causes combination between lead oxide and silica. If copper is present in the ore, the sulphur is not all oxidised by roasting, but some is left to combine with the copper and form a matte. The roasted ore is then smelted in the blast-furnace with coke and a flux consisting essentially of iron itself or compounds of iron. The iron may be in the form of ore, which may or may not have been originally associated with the lead, or in the form of basic iron silicates derived from the refining

or puddling of iron, or from copper smelting. In the smelting process some of the lead oxide is directly reduced by the carbon of the fuel, but for the most part the iron is first reduced, and this in turn reduces the lead. Moreover, if lead sulphide is present metallic iron will react with it, forming iron sulphide and metallic lead; the iron will also decompose lead silicate, liberating the metal. And since material poor in lead can be smelted in this furnace, the grey slags formed by the smelting of galena in the reverberatory furnace may be reduced here.

The slag should consist of the silicates of iron, calcium, aluminium, and magnesium, and not contain more than 3 per cent. of lead; if, however, sulphur was still present in the ore, there will also be a matte or regulus of sulphides of lead, iron, and copper, together sometimes with silver and gold. The matte is resmelted to remove the lead and concentrate the copper. Lead obtained from matte, however, is very impure.

*The Condensation of Lead Fume.*—Owing to the volatility of lead some of it is carried away and oxidised in the gases passing from the different furnaces employed in the extraction and purification of the metal. Various compounds of lead with other products are deposited when these gases cool, and constitute "lead fume." This "fume" consists chiefly of lead oxide and sulphate, together with smaller quantities of lead sulphide, ferrous oxide, alumina, zinc oxide, lime, and insoluble matter, and various arrangements have been adopted to collect this fume, and resmelt it. The method usually employed is to connect to the furnaces long flues which may be as much as 8 feet by 9 in cross-section, and from three to five miles long. Jets of water or steam may be made to enter the flues at intervals to assist precipitation of the fume; or a filtering arrangement of faggots, gauze, sawdust, or canvas bags, known as "bag houses," may be employed. An alternative method—that of Messrs. Wilson and French—is to pass the fume-laden gases, after cooling, through a condenser containing water in which the fume is deposited. The sludge is then removed to a settling tank, where the fume is separated from most of the water. It is subsequently dried and smelted in a blast-furnace.

(iii) **The Precipitation Process.** This "process of affinity," which consists of the reaction



plays some part in the smelting of lead in the blast-furnace already described; otherwise it is of relatively small importance. It has, however, been employed in France for the reduction of Spanish galena in a reverberatory furnace, but is said to be wasteful and expensive.

## PURIFICATION OF LEAD

Pig lead, obtained by any of the above processes, contains a number of impurities; these may be antimony, arsenic, copper, zinc, iron, tin, bismuth, silver, nickel, cobalt, and sulphur. The general effect of these impurities is to harden the lead; silver, moreover, may be recovered economically from the lead, much of this metal being now obtained from argentiferous galena.

There are, therefore, two distinct branches of lead purification: softening and desilverisation.

**Softening of Lead.**—There are two processes of softening: liquation and oxidation. The process of liquation, which is employed especially to diminish copper, consists in carefully heating the crude metal on the sloping bed of a reverberatory furnace. A pure lead melts and runs away, leaving behind an alloy which contains the copper together with nickel and cobalt, and sometimes arsenic and sulphur.

Other impurities are removed by oxidation. The metal is melted in a reverberatory furnace, and exposed at a red heat to the action of air. A scum forms on the surface, consisting of the more oxidisable impurities together with some oxide of lead; lime is sometimes added to stiffen the scum, which is removed from time to time, and the molten lead beneath it is tested at intervals, so that the process may be continued until oxidation of impurities is complete. The first oxidation products contain most of the tin, later ones the antimony. Bismuth is not removed in this way, since it is not more oxidisable than lead; but it is associated with the silver in the Pattinson process for desilverisation.

**Desilverisation of Lead.**—Originally the only process available for recovering silver from argentiferous lead was that of cupellation, by which all the lead was oxidised, and so needed again to be reduced to metal. Now three other processes are in use, which are associated with the names of Pattinson, Rozan, and Parker.

**The Pattinson Process.** This process, sometimes spoken of as Pattinsonising or Pattinsonage, was invented by Hugh Lee Pattinson, of Newcastle-on-Tyne, who took out a patent, in October 1833, for "An improved method of separating silver from lead." The method depends upon the fact that when an alloy of lead with not more than 1·8 per cent. of silver is melted, and allowed to cool slowly, pure lead crystallises out, leaving a molten alloy richer in silver. The principle of the process is the same as that according to which pure ice separates when a dilute aqueous solution of a substance is sufficiently cooled. Moreover, pure lead is denser in the solid than in the liquid state, and therefore sinks to the bottom of the molten alloy.

The process is carried out in a series of iron pans, each heated over a fire. The lead is melted in the first pan, skimmed, and then allowed to cool; the sprinkling of water on the surface helps the cooling. As solid lead separates it is pushed beneath the surface of the molten metal, so that it may redissolve if possible. After a time crystals of lead accumulate at the bottom of the pan and are then removed by a perforated ladle, allowed to drain from the liquid argentiferous lead on their surface, and then placed in the next pan, which has already been made hot enough to melt them. In this way two-thirds, or even as much as seven-eighths, of the metal is removed from the first pan, leaving behind a correspondingly enriched alloy. In practice alternate pans of different qualities are generally being crystallised simultaneously, and the rich remainder of one pan is mixed in the intervening pan with the poorer lead from the other pan. By successive crystallisations and removals of lead from the various pans, the original alloy is gradually separated into purified lead at one end of the series of pans, and an enriched alloy at the other end. So from a lead containing only 10 ounces of silver per ton, a rich alloy containing from 600 to 700 ounces per ton is separated; this is then cupelled. The Pattinson



process is generally employed for lead too poor in silver to be profitably dealt with by any other process.

**The Rozan Process or Pattinsonising by Steam.**—This process, introduced in the works of Luce and Rozan at Marseilles, has been described by Cookson.<sup>1</sup> Two pots only are required, a melting pot and a crystallising pot. The molten alloy, after removal from the melting to the crystallising pot, is stirred up in the latter by high-pressure steam, while the surface of the metal is cooled by water. About two-thirds of the lead is allowed to crystallise, and then the still liquid alloy is drained off from the crystals through spouts protected by perforated plates, which prevent solid lead from leaving the pot. Another charge of lead, of silver content equal to that of the crystals remaining in the crystallising pot, is added from the melting pot, the whole remelted, and the operation repeated. It is claimed for this process that it obviates the need for previous softening of the lead, since the steam, either itself, or by the air it carries into the pot, causes the oxidation of impurities; also that its use effects a great saving in labour, fuel, and the amount of dross formed.

**The Parkes Process: Desilverisation by Zinc.** Molten lead and zinc are partially miscible liquids, like water and ether. Equilibrium is established between the two liquids when the lead has dissolved 1·6 per cent. of zinc, and the zinc 1·2 per cent. of lead. It was observed by Karsten in 1842 that silver is more soluble in molten zinc than in molten lead, so that zinc when melted with argentiferous lead will remove and dissolve its silver; just as, for example, aniline is more soluble in ether than in water, and ether when shaken with water containing aniline will consequently dissolve out the aniline.

Practical use was made of these facts by Alexander Parkes, of Birmingham, who, in the years 1850 to 1852, took out patents for the desilverisation of lead by zinc.

The lead is melted in one of a series of pots, and heated to the melting-point of zinc. Slabs of zinc are then added, and the contents of the pot are stirred until the zinc is melted. The amount of zinc used varies between  $1\frac{1}{2}$  and 2 per cent. of the lead, according to the quantity of silver present; and it is generally added in three successive quantities, the separated and solidified zinc, containing the silver, being removed to a smaller pot before more zinc is added.

The zinc remaining in the desilverised lead is removed by oxidation with air or steam, followed by skimming; or by the aid of an alloy of copper or copper-aluminium with lead,<sup>2</sup> which takes up the zinc and forms a crust on the surface of the lead. The zinc is then recovered from the alloy by distillation.

From the zinc-silver alloy, some of the lead that it contains is removed by liquation. The alloy is then heated in a fire-clay retort, by which means the zinc is distilled and recovered; and the rich silver-lead alloy remaining is then cupelled.<sup>3</sup>

If gold and copper are present in market lead they are also separated from it by the Parkes process.

**Electrorefining of Lead.**—Lead is refined by electrolysis, impure lead being made the anode, and a thin slab of pure lead the cathode,

<sup>1</sup> Cookson, *Trans. Newcastle Chem Soc.*, 1878.

<sup>2</sup> Coda, *German Patent No. 207,104*.

<sup>3</sup> For a description of cupellation, see under Silver, this series, vol. II.

in a cell containing a suitable lead solution as the electrolyte. The most successful process is that of Betts,<sup>1</sup> wherein the electrolyte consists of a solution of lead silicofluoride, formed by dissolving the carbonate in aqueous hydrofluosilicic acid, to which is added 1 part of gelatine in 5000 in order to secure a coherent deposit of lead. The electro-deposition of lead is also very satisfactorily carried out by the employment of a solution of the perchlorate.<sup>2</sup>

### PROPERTIES AND USES OF LEAD

**Physical Properties of Lead.** Lead is bluish grey, and when unoxidised has a bright, shining appearance, well seen in the crystals separated from a lead salt solution by zinc, in the formation of the so-called lead-tree. Lambert and Culh.<sup>3</sup> have prepared pure lead by the method of Stas,<sup>4</sup> and distilled it in a vacuum in a silica tube. The globules of metal obtained had a very brilliant lustre, resembling that of mercury or silver, the bluish tint usually associated with lead being entirely absent from them. The fresh surface of the metal rapidly becomes dull owing to oxidation, probably with the formation of the suboxide,  $Pb_2O$ , and then presents the appearance ordinarily associated with lead. Lead is dimorphous, crystallising in the regular and monoclinic systems. Regular octahedra are produced when the molten metal solidifies, and are best obtained by allowing a crust to form and then pouring away the still liquid metal. From the state of vapour lead crystallises in combinations of the regular octahedron and cube.<sup>5</sup> Plates, which appear to be monoclinic, are formed by the electrolysis of solutions of lead salts by feeble currents, but when strong currents are employed octahedral crystals separate. According to Ellis and Rixon,<sup>6</sup> lead may be deposited during electrolysis, either in shining plates or as a sponge of microscopic needles, the spongy deposit being due to the presence of plumbic salt in the electrolyte. In the growth of the lead-tree, however, when a rod of zinc is immersed in a solution of lead acetate, the separation of plates is frequently followed by the appearance of a spongy deposit. A layer of spongy lead is formed on the cathode during the electrolysis of sulphuric acid with lead electrodes.<sup>7</sup>

The density of lead has been determined under various conditions. Lead that has been poured while molten into water has a density of 11.352 at 0° C. compared with water at 4° C., and thus when the metal has been rolled becomes<sup>8</sup> 11.358-11.365. When distilled in a vacuum lead has a density of 11.3415 at 20° C., which when the metal is submitted to a pressure of 10,000 atmospheres becomes<sup>9</sup> 11.3470. Cohen and Helderman<sup>10</sup> have found the density of pure lead at 25° C. compared with water at 4° C. to be 11.3299. At its melting-

<sup>1</sup> *Lead Recovery by Electrolysis*, by A. G. Betts (J. Wiley and Sons, 1908).

<sup>2</sup> Mathers, *Chem. Zeit.*, 1910, 34, 1316, 1350, *Trans. Amer. Electrochem. Soc.*, 1910, 17, 261.

<sup>3</sup> Lambert and Culh., *Trans. Chem. Soc.*, 1915, 107, 210.

<sup>4</sup> Stas, *Bull. Acad. roy. Belg.*, 1890, 10, 293.

<sup>5</sup> Kahlbaum, Roth, and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 177.

<sup>6</sup> Ellis and Rixon, *Zeit. Elektrochem.*, 1903, 9, 267.

<sup>7</sup> Haber, *Zeitsch. anorg. Chem.*, 1898, 16, 438.

<sup>8</sup> Reich, *J. prakt. Chem.*, 1859, 78, 328.

<sup>9</sup> Kahlbaum, Roth, and Siedler, *loc. cit.*

<sup>10</sup> Cohen and Helderman, *Zeitsch. physikal. Chem.*, 1915, 89, 733.

point (325° C.) the density of the solid metal is 11.005, and of the liquid metal 11.645,<sup>1</sup> whence it appears that lead expands on solidifying. Lead melts at about 327° C.; Heycock and Neville<sup>2</sup> found 327.6° C., Callendar,<sup>3</sup> 327.7° C., and Holborn and Day,<sup>4</sup> 326.9° C. When contained in a quartz tube in a cathode light vacuum lead<sup>5</sup> begins to evaporate at about 1000° C.; under a short vapour column it boils at 1140°–1142° C., whilst under a pressure of 45 mm. its boiling-point is 1172–1173° C. Lead vapour is monatomic<sup>6</sup> at 1870° C.; the metal is also monatomic in solution in mercury.<sup>7</sup>

The spectrum of lead has been examined by Hartley, Hagenbach, and Koenen, Lamprecht,<sup>8</sup> and Klein.<sup>9</sup>

The most intense lines in the spectrum of lead are as follow<sup>10</sup>:

Arc : 2393.92, 2577.39, 2614.26, 2663.27, 2802.10, 2823.31, 2833.21, 2873.18, 3572.95, 3639.72, 3671.80, 3683.62, 3740.20, 4019.80, 4058.00, 5005.63.

Spark : 2802.10, 2833.12, 3573.03, 3639.72, 3683.64, 3740.28, 4058.00, 4245.42, 4387.11, 5609.00.

Lead is the softest of the common metals; it may be easily cut with a knife, and leaves a streak when rubbed upon paper. In Moh's scale of hardness (diamond = 10) lead is 1.5. Lead is tough and malleable, and so can be rolled out into thin foil; it cannot, however, be drawn into fine wire, and lead wire of the thickness of fine string can very easily be snapped. Pieces of lead foil can be welded together under a pressure of 2000 atmospheres.<sup>11</sup>

Lead becomes harder and more brittle when alloyed with antimony, zinc, bismuth, or arsenic. The last-named metal is present in shot. The specific heat of lead has been the subject of numerous investigations.<sup>12</sup> The following results were obtained by Naccari,<sup>13</sup> at temperatures between 18° C. and 300° C.:

18° C.	50° C.	100° C.	150° C.	200° C.	250° C.	300° C.
0.02993	0.03010	0.03108	0.03176	0.03211	0.03312	0.03380

It will be seen from these figures that lead obeys Dulong and Petit's law,<sup>14</sup> since atomic weight  $\times$  specific heat = 207  $\times$  0.03 = 6.21.

Colloidal lead is obtained by reducing lead chloride solution with hydrazine in the cold.<sup>15</sup>

**Allotropy of Lead.** Until recently no allotropic form of lead had been recognised. It has been observed, however, by Cohen and Helder-

<sup>1</sup> Vicentini and Omodei, *Ann. Physik. Beibl.*, 1888, 12, 176.

<sup>2</sup> Heycock and Neville, *Trans. Chem. Soc.*, 1894, 65, 65.

<sup>3</sup> Callendar, *Phil. Mag.*, 1899, [v], 48, 519.

<sup>4</sup> Holborn and Day, *Ann. Phys.*, 1900, [iv], 2, 505.

<sup>5</sup> Kraft, *Ber.*, 1903, 36, 1690.

<sup>6</sup> Von Wartenberg, *Zeitsch. anorg. Chem.*, 1908, 56, 320.

<sup>7</sup> G. Meyer, *Zeitsch. physikal. Chem.*, 1891, 7, 477. Ramsay, *ibid.*, 1889, 3, 359.

<sup>8</sup> Lamprecht, *Zeitsch. wiss. Photochem.*, 1911, 10, 16, 33.

<sup>9</sup> Klein, *Zeitsch. wiss. Photochem.*, 1913, 12, 16.

<sup>10</sup> Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and Wien, 1911).

<sup>11</sup> Spring, *Ann. Chim.*, 1881, [v], 22, 184.

<sup>12</sup> Bartoli and Stracanti, *Rend. Ist. Lomb.*, 1895, ii, 28; Le Verrier, *Compt. rend.*, 1892, 114, 907; Behn, *Wied. Annalen*, 1898, 66, 237; Schmitz, *Proc. Roy. Soc.*, 1903, 72, 177; Tomlinson, *Proc. Roy. Soc.*, 1881, 37, 109; Spung, *Bull. de Belg.*, 1886, [iii], 11, 355.

<sup>13</sup> Naccari, *Atti R. Accad. Sc. Torino*, 1887–8, 23, 107, *Gazzetta*, 1888, 18, 13.

<sup>14</sup> See this series, vol. i, p. 89.

<sup>15</sup> Gutbier, *Zeitsch. anorg. Chem.*, 1902, 31, 448.

man<sup>1</sup> that when pure lead is immersed in a solution of lead acetate containing nitric acid the metal undergoes a structural change accompanied by a change of density. These facts are believed to indicate that ordinary lead consists of a metastable mixture of several allotropic modifications of the metal. Heller<sup>2</sup> also found that pure lead becomes brittle after immersion in an acidified solution of lead acetate or nitrate for several days, and called the new form of metal "grey lead." Coughton<sup>3</sup> has obtained a similar result by passing an electric current through nitric acid of density 1.12, with the  $\beta$  lead as cathode, and platinum foil as anode; after cathodization the cathode became grey, soft, and powdery. Laity, Cohen, and Helderum<sup>4</sup> observed that pure lead suspended in a 10 per cent. solution of lead acetate, containing 100 c.c. of 1.16 nitric acid per litre, showed rises due to contraction; the changed lead is believed to be composed of several allotropic forms. Jancke<sup>5</sup> has confirmed the existence of allotropic forms of lead by the study of pressure-temperature curves of the metal.

Lambert and Culhs<sup>6</sup> also attribute to allotropy certain phenomena connected with the action of water and oxygen on pure lead.

Lead is now definitely recognized as a denaturation product of radium, and radium D has been obtained in visible quantity and proved to be chemically identical with lead.<sup>7</sup>

**Chemical Properties of Lead.** The key to the chemical behaviour of lead is furnished by the position this element occupies in the electro-potential series of the metals. In this series lead occupies a position close to that of tin, and little removed from that of hydrogen, both these metals being slightly more electropositive than hydrogen. It has been found that against a normal hydrogen electrode lead shows a potential of  $-0.120$  volt. Consequently lead possesses very little power of displacing hydrogen from aqueous solutions of acids, and this power is sometimes interfered with by the insolubility of the products of the action. Thus lead dissolves in hydrochloric acid with more difficulty than tin, although lead possesses a greater solution pressure than tin.

A chemical comparison of lead and tin has been carried out by Sackin,<sup>8</sup> who finds that while lead precipitates tin from nitric acid solution, it is precipitated from acetic acid solution by tin. A condition of equilibrium between the two metals consistent with the law of mass action is attained in the case of solutions in hydrochloric and sulphuric acids. The conclusion is reached by measurements of the E.M.F. of a voltaic element of the form  $\text{Pb} | \text{Pb}(\text{NO}_3)_2 | \text{Sn}(\text{NO}_3)_2 | \text{Sn}$  that the electrolytic solution tension of lead is about 17.2 times as great as that of tin. This great difference, which is partly accounted for by the feeble ionisation of standard salts, is in accordance with the relative positions of the two elements in the periodic system, and the stronger basic properties of lead oxide, as shown by the stabilities of its oxy-salts. Since lead is so little capable of displacing hydrogen

<sup>1</sup> Cohen and Helderum, *Proc. Kon. Akad. Wetensch. Amsterdam*, 1914, 17, 822.

<sup>2</sup> Heller, *Z. Elektrochem.*, 1913, 35, 764.

<sup>3</sup> Coughton, *Amer. Chem. Soc.*, 1915, 37, 544.

<sup>4</sup> Cohen and Helderum, *Goldschmidt Ber.*, 1915, 89, 733.

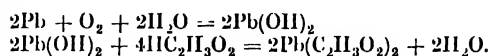
<sup>5</sup> Jancke, *Z. physikal. Chem.*, 1916, 90, 313.

<sup>6</sup> Lambert and Culhs, *Trans. Chem. Soc.*, 1915, 107, 210.

<sup>7</sup> Von Heyes and Panch, *Ber.*, 1914, 47, 2781.

<sup>8</sup> Sackin, *Chem. Zentr.*, 1904, 1, 863.

from dilute acids, its solution by such an acid as acetic acid is to be attributed chiefly to the assistance of atmospheric oxygen in the sense of the reactions :



Tin, which is not so oxidisable as lead, is not attacked by acetic acid. The great difference in behaviour between lead and tin towards water containing dissolved air must be attributed to the same cause.

Lead reacts vigorously with fluorine, and with diminishing vigour towards the other halogens in turn. Finely divided lead, produced by heating lead tartrate out of contact with air, is pyrophoric. Ordinary lead in the air becomes coated with a film of the suboxide,  $\text{Pb}_2\text{O}$ , which is also formed as a grey film on the surface of molten lead. By exposure to red heat, however, lead is converted into the monoxide, as in the process of cupellation.

Boiling water is appreciably decomposed by granulated lead,<sup>1</sup> and lead monoxide is reduced by hydrogen; thus the reaction is a reversible one proceeding to an equilibrium at a given temperature. Some what diluted nitric acid is the best solvent for lead, and the oxides of nitrogen evolved contain a larger proportion of nitric oxide than in the case of copper.<sup>2</sup> The presence of much sulphuric acid modifies the interaction of nitric acid and lead, causing reduction to nitrous acid; and when dilute nitric acid is electrolysed with lead electrodes in presence of upwards of 10 per cent. of sulphuric acid, about 40 per cent. of the nitric acid is converted into hydroxylamine.<sup>3</sup>

Concentrated sulphuric slowly attacks lead in the cold, and when the acid is heated a vigorous reaction sets in, with evolution of hydrogen, sulphur dioxide, and hydrogen sulphide. Sulphuric acid of density 1.760 and upwards attacks the lead pans in which it is evaporated at a temperature of about 200° C. in sulphuric acid manufacture; and the lead sulphate formed dissolves in the acid, whence it is precipitated on dilution. Pure lead is less affected than the impure metal, but the action varies with the nature of the impurity and the physical condition of the metal.<sup>4</sup>

**Composition and Uses of Commercial Lead.**—Owing to the purifying treatment to which the metal is submitted, commercial lead attains a high degree of purity. The foreign metals generally present are copper, antimony, iron, zinc, and silver, with less frequently bismuth, and occasionally a minute trace of tin and arsenic. The total metallic impurity, however, rarely exceeds 0.1 per cent., and may fall below 0.01 per cent.

Lead was employed in olden times for making cisterns and coffins, and as a roofing material for important buildings, such as churches. At the present day it is likewise employed for the purposes included in the art of the plumber, in the form of sheets and in pipes for conveying water and gas. It is also used, on account of its power of resisting the action of acids, for the manufacture of chemical plant, such as

<sup>1</sup> Regnault, *Ann. Chim. Phys.*, 1836, [n], 62, 337; Stohba, *J. prakt. Chem.*, 1865, 94, 113.

<sup>2</sup> Higley, *Amer. Chem. J.*, 1895, 7, 18.

<sup>3</sup> Tafel, *Zeitsch. anorg. Chem.*, 1902, 31, 289.

<sup>4</sup> Hart, *J. Soc. Chem. Ind.*, 1907, 26, 504.

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sulphuric acid chambers. It has been found, however, that for this purpose ordinary lead is better than the purest metal. Further, lead is used in accumulators, for making solders, pewter, type-metal, etc., and when alloyed with arsenic, added in the form of white arsenic or arsenical dross, for the manufacture of shot. The arsenic increases the fluidity of the molten metal, as well as the tendency of its drops to become spherical as they pass through the air. Shot is made by dropping the molten metal through colanders pierced with holes, down a tower or well into water. The size of the shot depends not only on the size of the holes in the colander, but on the initial temperature of the metal, and the height through which the drops are made to fall. The shot is sorted by sifting, and by rolling down an inclined metal plane, the imperfectly shaped shot thus remaining on the plane. Finally, the shot is polished with plumbago.

## ALLOYS OF LEAD

The most important alloys of lead are those with tin, which have already been described under the latter metal. Numerous binary and ternary alloys of lead with other metals have, however, been prepared for purposes of metallographic study.

The following bibliography of the alloys of lead may prove useful to the reader.<sup>1</sup>

## BIBLIOGRAPHY OF ALLOYS OF LEAD

ALLOYING ELEMENT	REFERENCE
Aluminum	Peckens, <i>Compt. rend.</i> , 1904, 138, 101; 1906, 143, 397 Gawer, <i>Zentralblatt Chem.</i> , 1908, 57, 113
Antimony	Gawer, <i>ibid.</i> , 1906, 58, 119 Strobel and Kopp, <i>Ann. d. Russ. Phys. Chem. Soc.</i> , 1906, 30, 901 Howard, <i>J. Phys. Chem.</i> , 1908, 30, 368 Howard, <i>ibid.</i> , 1913, 156, 1561
Antimony and arsenic	Howard, <i>J. Phys. Chem.</i> , 1908, 30, 1789
Arsenic	Landolt, <i>Metall.</i> , 1906, 5, 11 Howard, <i>ibid.</i> , 1914, 6, 49
Bismuth	Landolt, <i>ibid.</i> , 1910, 35, 391
Bismuth and cadmium	Howard, <i>J. Phys. Chem.</i> , 1910, 32, 1390
Cadmium and zinc	Neck, <i>Zentralblatt Chem.</i> , 1905, 47, 121
Cadmium and mercury	Landolt, <i>Zentralblatt Chem.</i> , 1910, 35, 328
Calcium	Hack, <i>ibid.</i> , 1906, 143, 227 Donati, <i>Zentralblatt Chem.</i> , 1908, 57, 185 Howard, <i>ibid.</i> , 1911, 70, 362
Cobalt	Donati, <i>ibid.</i> , 1908, 57, 362 Howard, <i>Zentralblatt Chem.</i> , 1908, 59, 293
Copper	Newton and Gilbert, <i>J. Physical Chem.</i> , 1911, 18, 70
Copper and nickel	Parravano and Mezzetti, <i>ibid.</i> , 1911, 44, 375
Copper and silver	Landolt and Lecons, <i>Metallurg.</i> , 1907, 4, 293
Copper and zinc	Parravano, Mezzetti, and Monetti, <i>ibid.</i> , 1911, 44, 375
Gold	Vogel, <i>Zentralblatt Chem.</i> , 1907, 45, 11

<sup>1</sup> For references to alloys of lead alloys containing tin, see p. 340. Lead amalgams are dealt with by Fay and North, *Amer. Chem. J.*, 1901, 25, 216.

ALLOYING ELEMENT	REFERENCE
Indium	Kurnakoff and Puschin, <i>J. Russ. Phys. Chem. Soc.</i> , 1906, 38, 1146
Magnesium	Grube, <i>Zeitsch. anorg. Chem.</i> , 1905, 44, 117 Kurnakoff and Stepanoff, <i>ibid.</i> , 1905, 46, 177 Stepanoff, <i>ibid.</i> , 1908, 60, 209
Manganese	Williams, <i>ibid.</i> , 1907, 55, 1
Mercury	Richards and Garrod-Thomas, <i>Zeitsch. physikal. Chem.</i> , 1910, 72, 165
Nickel	Portevin, <i>Rev. Metallurg.</i> , 1907, 4, 814 Voss, <i>Zeitsch. anorg. Chem.</i> , 1908, 57, 34
Palladium	Ruef, <i>ibid.</i> , 1907, 52, 315 Puschin and Pashsky, <i>J. Russ. Phys. Chem. Soc.</i> , 1908, 40, 826
Platinum	Dornickel, <i>Zeitsch. anorg. Chem.</i> , 1907, 54, 333 Puschin and Laschtschenko, <i>ibid.</i> , 1909, 62, 34
Potassium	Smith, <i>ibid.</i> , 1907, 56, 109
Silicon	Tamura, <i>ibid.</i> , 1909, 61, 40
Silver	Friedrich and Puchter, <i>Metallurg.</i> , 1906, 3, 396 Petrenko, <i>Zeitsch. anorg. Chem.</i> , 1907, 53, 200
Silver and zinc	Morssin and Watrinbe, <i>Compt. rend.</i> , 1907, 144, 16 Kriemann and Holmeyer, <i>Monatsh.</i> , 1911, 32, 597 Bogitch, <i>Compt. rend.</i> , 1911, 159, 178
Sodium	Mathewson, <i>Zeitsch. anorg. Chem.</i> , 1906, 50, 171
Tellurium	Fay and Gillson, <i>Amer. Chem. J.</i> , 1902, 27, 81
Thallium	Lewkonja, <i>Zeitsch. anorg. Chem.</i> , 1907, 52, 152 Kurnakoff and Puschin, <i>J. Russ. Phys. Chem. Soc.</i> , 1906, 38, 1146

**Physiological Action of Lead.** Lead compounds are poisonous, especially when soluble. Lead-poisoning is cumulative, that is to say successive minute quantities, which separately might be innocuous, produce serious or fatal effects after a time, owing to their accumulation in the body. Indeed, a single large dose of a lead compound is less dangerous than repeated small doses, and seldom proves fatal. Chronic lead-poisoning may result from the drinking of water containing lead derived from the pipes in which the water has been conveyed; or from the continued handling of lead compounds, such as white lead. Those engaged in the manufacture of these compounds may be affected, as well as those who use them, especially painters, and pottery workers employing white lead for glazing purposes.

The symptoms of lead-poisoning are general ill-health with loss of appetite, interference with digestion, accompanied by abdominal pains (painters' colic), constipation, nervous prostration, epileptic fits, local paralysis, especially of the wrists, known as "dropped-wrist," followed by general paralysis and death. Signs of such poisoning are seen in the blue line which appears at the edges of the gums, owing to the deposition there of lead sulphide. Occasionally also the teeth turn black, and the skin assumes a jaundiced hue. The lead is distributed in various parts of the body, and is partially excreted by the kidneys. Potassium iodide is said to aid this elimination.

**Action of Water on Lead.**—On account of the employment of metallic lead for the lining of cisterns and construction of pipes for storing and conveying potable water, the action of such water upon lead is of great importance, and has been fully investigated.

Pure water from which air is excluded is practically without action on lead at ordinary temperatures, since lead was found in such water only to the extent of 0.3 part per million.<sup>1</sup>

The action of water and oxygen on carefully purified lead has been examined by Lambert and Cullis.<sup>2</sup> The distilled metal was submitted to the action of pure water with and without the addition of pure oxygen. The action of pure water on the fresh surface of the metal was unappreciable, but on the addition of pure oxygen very rapid corrosion took place, with the formation first of hydrated plumbous oxide,  $\text{Pb}_2\text{O} \cdot 2\text{H}_2\text{O}$ , and then the ordinary white crystalline lead hydroxide. When the pure distilled metal has been kept for some months it becomes much less oxidisable, so that it may be exposed to ordinary air for many days without any appreciable loss of its brilliant lustre. This difference in oxidisability between the recently and earlier distilled metal is attributed by Lambert and Cullis to allotropy, a metastable, more active form of the metal being first produced when the vapour condenses.

The allotropy of lead also serves to account for the action of water and oxygen on the metal, which, according to Lambert and Cullis, originates in electrical action due to differences of potential between different parts, for in the purified metal such differences must necessarily be attributed to physical and not chemical heterogeneity. Thus pure water is supposed to initiate action on pure lead with the separation of hydrogen, and the formation of plumbous ions in solution; but this action is quite unappreciable until oxygen is added to oxidise and remove the hydrogen which offers an enormous resistance to the passage of the current.

Hydrogen peroxide, which is formed during the wet oxidation of lead,<sup>3</sup> is said by Lambert and Cullis to be the product of a subsidiary action, and to have no direct bearing on the process of corrosion. It is responsible, however, for oxidising lead monoxide to the higher oxides.

Water containing only dissolved oxygen acts more readily upon lead than water containing only dissolved carbon dioxide. This confirms the conclusion that the first action on lead of water containing dissolved air is one of oxidation, so that lead hydroxide is formed and passes into solution. Water containing carbon dioxide dissolved under pressure dissolves, however, large quantities of lead.<sup>4</sup> Lead hydroxide in solution subsequently reacts with carbon dioxide derived from the air with the formation and precipitation of a basic carbonate of the composition  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ .

The effect of various salts, present to the extent of 0.2 gram per litre, upon the solvent action of water on lead, was examined by Mur,<sup>5</sup> who placed them in the following order according to their action on the metal: ammonium nitrate, calcium chloride, ammonium sulphate, potassium nitrate, potassium carbonate; he also found that the solvent action was always the greater the more considerable the exposure to air. This difference is due to the different solubilities of basic lead carbonate in dilute solutions of these salts.

<sup>1</sup> Clowes, *Proc. Chem. Soc.*, 1902, 18, 46.

<sup>2</sup> Lambert and Cullis, *Trans. Chem. Soc.*, 1915, 107, 210.

<sup>3</sup> Traube, *Zetsch. physikal. Chem.*, 1900, 32, 137; Dortan, *Trans. Chem. Soc.*, 1911, 100, 1835.

<sup>4</sup> Mur, *J. Chem. Soc.*, 1877, 1, 660; see also Traube-Mengarini and Scala, *Atti R. Accad. Lincei*, [v], 18, 11, 111, and Heap, *J. Soc. Chem. Ind.*, 1913, 32, 771, 811, 817.

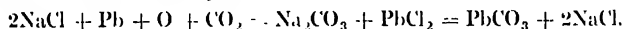


• Whilst ammonium nitrate in solution appears to exert on lead the greatest solvent action of any known salt, other nitrates show no considerable action, and sulphates, phosphates, carbonates, and silicates actually retard the solvent action of water. This is well shown when clean sheets of lead are immersed in ordinary distilled water and in tap water, contained in stoppered bottles, and allowed to stand side by side for some months. After some time the distilled water will contain basic carbonate in suspension, while the tap water will be clear, because in this case the action has been stopped by the formation of a protective crust of the salt on the surface of the lead.

The inhibitive action of chalk, sand, and old mortar on the corrosion of lead by water has long been recognised<sup>1</sup>; and it appears that the presence of 0.5 gram of dissolved silica per gallon is sufficient to render the water lead-proof. It has been found that the best way to prevent water from attacking lead is to bring it into contact with a mixture of flints and limestone. According to Carnelley and Frew,<sup>2</sup> this is owing to the formation of calcium silicate in solution. Water containing carbon dioxide dissolved under pressure dissolves considerable quantities of lead<sup>3</sup>; peaty waters, containing in solution organic acids, such as ulmic and humic acids, corrode lead; and free lime is particularly active in this respect. Indeed, it is known to plumbers that lead pipes laid in contact with new mortar are liable to corrosion. When water is to be tested for minute quantities of lead it must not be filtered through paper, which adsorbs the lead salts so that only a small proportion of them is found in the filtrate.

From a consideration of the kinds of impurity which cause water to dissolve lead, it will appear that a good potable water containing both temporary and permanent hardness in moderate amount, only a little nitrate, and no appreciable quantity of ammonium salt, has little or no effect upon lead; and, therefore, that such water may be safely conveyed in lead pipes.

**Decay of Objects made of Lead.**—Ancient lead objects kept in museums sometimes crumble to a fine powder, which consists essentially of lead carbonate, but also always contains chlorides. It was shown by Matignon<sup>4</sup> that a piece of lead which had been dipped in a 30 per cent. solution of sea salt, and then dried so as to become coated with salt crystals, underwent progressive destruction over a period of three years; but that a similar piece of lead which had not been so treated showed no destruction. Consequently it is believed that the following cycle of reactions takes place:



#### ATOMIC WEIGHT OF LEAD

In his list of atomic weights Dalton attributed to lead the value 95; this is really the equivalent referred to O = 7. Berzelius,<sup>5</sup> in 1811, took into account the three oxides of lead: litharge, red lead, and the peroxide; but since at this time no independent guiding principle

<sup>1</sup> *Report on the Action of Water on Lead* made to the Water Committee of the Corporation of Huddersfield in 1886.

<sup>2</sup> Carnelley and Frew, *J. Soc. Chem. Ind.*, 1888, vii, 15.

<sup>3</sup> Muir, *J. Chem. Soc.*, 1877, 31, 660.

<sup>4</sup> Matignon, *Compt. rend.*, 1912, 154, 1609.

<sup>5</sup> Berzelius, *Gilbert's Annalen*, 1811, 37, 252.

was known whereby to fix the magnitude of an atomic weight, no just conclusion could be drawn from the analysis of these compounds.

Berzelius was then of the opinion that the atomic weight of lead is 111, attributing to litharge the formula  $\text{PbO}$ . In 1826, however, on account of the generalisations of Dulong and Petit and Mitscherlich, he halved this value, and wrote  $\text{Pb} = 207$ ; nevertheless Gmelin, in the same year, because of the confusion in which fundamental principles were involved at that period, reduced the atomic weight to an equivalent, and adopted the round figure  $\text{Pb} = 101.00$ .

That the atomic weight of lead is approximately 207 is shown by the following facts:

(i) The specific heat of lead between  $18^\circ \text{C}$ . and  $100^\circ \text{C}$ . is 0.031 (Magnus). Assuming, according to Dulong and Petit's law, a mean atomic heat of 6.4, the atomic weight is about 207.

(ii) Mitscherlich's law of isomorphism provides additional confirmation of this magnitude, for lead salts are isomorphous with corresponding salts of the alkaline earth metals, and the complex fluorides  $\text{K}_2\text{HPbF}_6$  and  $\text{K}_2\text{HSnF}_6$ , as well as the complex chlorides  $\text{M}_2\text{PbCl}_6$  and  $\text{M}_2\text{SnCl}_6$ , are isomorphous.

(iii) Lastly, lead occupies an appropriate position in the Periodic Table, in which it has been placed on account of its atomic weight being 207.

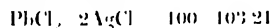
Analytical determinations of the atomic weight of lead were made by Berzelius,<sup>1</sup> Turner,<sup>2</sup> Anderson<sup>3</sup> and Svanberg,<sup>4</sup> Mangnag,<sup>5</sup> Dumas,<sup>6</sup> Stas,<sup>6</sup> Betts and Kern,<sup>7</sup> Baxter and Wilson,<sup>8</sup> Baxter and Thorvaldson,<sup>9</sup> and Baxter and Grover.<sup>10</sup>

The experiments of Mangnag were made upon lead chloride with the purpose of checking the atomic weight of chlorine. Two sets of gravimetric estimations were carried out in 1846 in which (a) lead was heated in an atmosphere of chlorine and was thus converted into the chloride, the ratio found being



whence  $\text{Pb} = 207.31$ .

(b) Lead chloride was dissolved in water and the chlorine precipitated by silver nitrate. The ratio found was



whence  $\text{Pb} = 206.81$ .

In 1859 Dumas obtained the ratio



whence  $\text{Pb} = 206.88$ .

The determination of the atomic weight of lead was included in

<sup>1</sup> Berzelius, *Föreläsning*, 5. Aufl., 3. bd., 1197, also 1187 and 1218.

<sup>2</sup> Turner, *Phil. Trans.*, 1833, 527, 538.

<sup>3</sup> Anderson and Svanberg, *Ann. Chem. Phys.*, 1843 [vol. 9, 241], *Repert. Chem.*, 1843, 27, 381.

<sup>4</sup> Mangnag, *Ann. Chem. Phys.*, 1846, 3, 186.

<sup>5</sup> Dumas, *Ann. Chem. Phys.*, 1859 [vol. 55, 129].

<sup>6</sup> Stas, *Œuvres Complètes*, 1860, 1, 384.

<sup>7</sup> Betts and Kern, *Trans. Amer. Electrochem. Soc.*, 1904, 6, 67.

<sup>8</sup> Baxter and Wilson, *J. Amer. Chem. Soc.*, 1908, 30, 187.

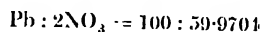
<sup>9</sup> Baxter and Thorvaldson, *J. Amer. Chem. Soc.*, 1915, 37, 1020.

<sup>10</sup> Baxter and Grover, *J. Amer. Chem. Soc.*, 1915, 37, 1027.

<sup>11</sup> For these and the succeeding values given for the atomic weight of lead the antecedent data are: O = 16.000, Cl = 35.457, Ag = 107.880, S = 32.065.

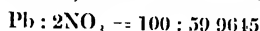
the classical researches of Stas. The work, which was published in 1860, comprised the conversion of pure lead into nitrate and sulphate respectively, the following results being obtained:

(a) The lead nitrate was ignited in a current of dry air at  $140^{\circ}\text{C}$ . to  $160^{\circ}\text{C}$ .



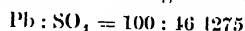
whence  $\text{Pb} = 206.79$ .

(b) The lead nitrate was ignited *in vacuo* at  $155^{\circ}\text{C}$ .



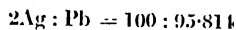
whence  $\text{Pb} = 206.81$ .

(c) With lead sulphate the following ratio was determined:



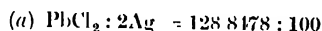
whence  $\text{Pb} = 206.91$ .

Betts and Kern determined, by an electrochemical method, the ratio

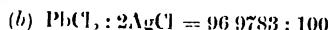


whence  $\text{Pb} = 206.73$ .

The above results are usually considered to be slightly too low for ordinary lead (*vide infra*, p. 383) and have been discarded in favour of the more accurate work of Baxter and Wilson. These investigators adopted a method similar to that of Margnau, the amount of silver, in the form of nitrate, required to precipitate completely a known weight of lead chloride was determined, as well as the weight of silver chloride produced. Special care was taken in the preparation of the lead chloride, which was made in different ways and recrystallised several times from hydrochloric acid solution in platinum vessels; and the specimens employed were required not to darken when heated in a stream of hydrogen chloride, and to form a clear solution in water after ignition. The ratios  $\text{PbCl}_2 : 2\text{Ag}$  and  $\text{PbCl}_2 : 2\text{AgCl}$  were determined, the former as the mean of nine, the latter as the mean of six experiments. The end point of the titration in the former experiments was determined by the use of the nephelometer.<sup>1</sup> The following results were obtained:



whence  $\text{Pb} = 207.089$

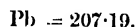


whence  $\text{Pb} = 207.097$ .

The mean value of the two sets of experiments is  $\text{Pb} = 207.093$ .

Subsequently Baxter and Thorvaldson carried out similar experiments with lead bromide prepared by precipitating lead nitrate solution with hydrobromic acid, and recrystallising the salt by dissolving it in hot concentrated hydrobromic acid, precipitating with water and drying it in a current of nitrogen and hydrogen bromide.

The two ratios  $\text{PbBr}_2 : 2\text{Ag}$  and  $\text{PbBr}_2 : 2\text{AgBr}$  were determined, and in each case the average was



In view of the discrepancy between the value  $\text{Pb} = 207.09$  obtained from lead chloride by Baxter and Wilson and the value  $\text{Pb} = 207.19$  obtained as above from the bromide, Baxter and Grover collected normal lead from various geographical and mineralogical sources,

<sup>1</sup> Greek *νεφέλη*, a cloud. See this series, vol. 1, p. 246.

purified it, and determined its atomic weight both by the bromide and the chloride method with the following results:

$\text{PbBr}_2 : 2 \text{Ag}$	Pb	207.20
$\text{PbBr}_2 : 2 \text{AgBr}$	Pb	207.18
$\text{PbCl}_2 : 2 \text{Ag}$	Pb	207.21
$\text{PbCl}_2 : 2 \text{AgCl}$	Pb	207.22

The mean value is Pb = 207.20, where Ag = 107.880, Br = 79.916, Cl = 35.457.

In consequence of these results the value **Pb = 207.20** has been adopted by the International Committee on Atomic Weights since 1916.

*The Atomic Weight of Lead from Radioactive Sources.* Until the development of the science of radioactivity the idea that the atomic weight of an "element" might vary according to its source had not entered the minds of chemists. If, however, the same "element" should be the final disintegration product of two other elements of different atomic weights which have passed through different stages of disintegration with loss of  $\alpha$ - and  $\beta$ -particles, the final "element" might exist in two *isotopic* forms, chemically indistinguishable, but differing from each other by several units of atomic weight.

Now Soddy and Hyman<sup>1</sup> have found that Ceylon thorite contains 0.39 per cent. of lead monoxide, whose lead is believed to be derived from the thorium in the mineral by radioactive change. Moreover, it has been calculated that the lead isotope derived from thorium should have an atomic weight of 208.4, since the thorium atom, of atomic weight 232.4, loses six helium atoms, of atomic weight 4, in the course of radioactive change. This is distinctly greater than the atomic weight of ordinary lead, Pb = 207.2.

Soddy and Hyman determined the atomic weight of thorite lead by the method of Baxter and Wilson, and found the values 208.5 and 208.3, with a mean value 208.4, which agrees with that indicated by the facts of radioactivity.

Equally striking were the results obtained by Richards and Lambert,<sup>2</sup> who, after confirming the accuracy of the value Pb = 207.1, as recognized by the International Atomic Weights Committee (1915), determined the atomic weights of lead obtained from a variety of radioactive minerals, with the following results:

Lead from North Carolina mammoth	206.40
Jochimsdal pitchblende	206.57
Colorado carnotite	206.59
Ceylonese thoranite	206.82
English pitchblende	206.86

Maurice Curie<sup>3</sup> has also obtained a somewhat analogous series of results with lead obtained from a variety of radioactive minerals, but unfortunately the sources of these are not specified:

Lead from carnotite	206.36
" vitro-tantalite	206.54
" pitchblende	206.64
" monazite	207.08
" galena	207.01

<sup>1</sup> Soddy and Hyman, *Trans. Chem. Soc.*, 1914, 105, 1402.

<sup>2</sup> Richards and Lambert, *J. Amer. Chem. Soc.*, 1914, 36, 1329. See also this series, vol. 1, p. 282.

<sup>3</sup> M. Curie, *Compt. rend.*, 1914, 153, 1675.

Hönigschmid and Mlle. St. Horovitz<sup>1</sup> found the value 206.736 as the mean of nine determinations of the atomic weight of purified lead that had been obtained from pitchblende; and, subsequently, by employing 20 kilos of selected purest Joachimsthal pitchblende, and also pure reagents, found the atomic weight of uranium-lead to be 206.105. Still more remarkable is the value  $206.046 \pm 0.014$  obtained by Marekwald from a uranium ore occurring in an old primary geological formation in Morogoro, East Africa; and with this must be placed the value  $206.063 \pm 0.008$  determined by Hönigschmid and Mlle. Horovitz<sup>2</sup> in a sample of broggerite from Moos, Norway, whilst the atomic weight of common lead determined in the same way, was found to be  $207.180 \pm 0.006$ . The arc and spark spectra of the two leads were, however, absolutely identical.<sup>3</sup>

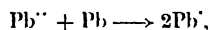
It has been pointed out by Soddy<sup>4</sup> that whilst the atomic weight of lead from thorium minerals should be greater than that of ordinary lead—viz.  $232.4 - 6 \times 4 = 208.4$ —the atomic weight of lead from uranium minerals should be less—viz.  $238.2 - 8 \times 4 = 206.2$ , that the extreme values found for the atomic weight of lead from these sources are 207.77 and 206.08 respectively; and that the densities of these two products are 11.376 and 11.273 respectively, the atomic volume of lead being the same whatever its source.

These are the first occasions in which the atomic weight of an element has been found to vary with its geographical source, and further researches along these lines will be awaited with interest.

The results clearly confirm the views of Russell,<sup>5</sup> Fajans,<sup>6</sup> and Soddy<sup>7</sup> on the significance of radioactive change in reference to the Periodic System.

### COMPOUNDS OF LEAD

Lead forms two well-defined classes of compounds derived respectively from the bivalent ion  $\text{Pb}^{++}$ , and the quadrivalent ion  $\text{Pb}^{4+}$ . In addition to these compounds there is the suboxide  $\text{Pb}_2\text{O}$ , which appears to be a representative of univalent lead. There is evidence, moreover, of the existence of univalent lead ions in solution; for it has been shown by Denham and Allmand<sup>8</sup> that a solution of lead acetate, heated with lead, forms a subacetate with the absorption of heat, thus:



and that a piece of lead in a solution of lead acetate which is maintained at two different temperatures forms a thermo-cell, the current flowing from the hot solution to the cold, and causing the deposition of traces of spongy lead at the cold end of the column of lead. The anomalous behaviour of the hydrogen electrode in solutions of lead salts is attributable to the reduction of the bivalent

<sup>1</sup> Hönigschmid and Mlle. Horovitz, *Compt. rend.*, 1914, 158, 1796.

<sup>2</sup> Hönigschmid and Mlle. Horovitz, *Monatsh.*, 1915, 36, 355.

<sup>3</sup> See also Merton, *Proc. Roy. Soc.*, 1916, A, 91, 198.

<sup>4</sup> Soddy, *Nature*, 1917, 98, 469.

<sup>5</sup> A. S. Russell, *Chem. News*, 1913, 107, 49.

<sup>6</sup> Fajans, *Physikal. Zeitsch.*, 1913, 14, 131, 136; *Lier.*, 1913, 46, 422; *Ber. deut. physikal. Ges.*, 1913, 15, 240; *Le Reclum.*, 1913, 10, 171.

<sup>7</sup> Soddy, *Chem. News*, 1913, 107, 97; *Jahrb. Radioakt. Elektronsk.*, 1913, 10, 188.

<sup>8</sup> Denham and Allmand, *Trans. Chem. Soc.*, 1908, 93, 424.

# LEAD AND ITS COMPOUNDS

lead ion to a univalent ion, just as the discrepancy observed in copper and silver voltameters is due to the formation of subsalts of these two metals. The following are the chief compounds of lead

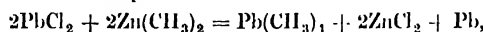
## CHIEF COMPOUNDS OF LEAD

	Univalent	Bivalent	Quadrivalent
Alkyls			
Fluorides		$PbF_2$	$Pb(CH_3)_4$ , $Pb(C_2H_5)_4$ etc
Chlorides		$PbCl_2$ , double and basic salt	$PbCl_4$ , $K_2HPbCl_6$ , $PbCl_4 \cdot (NH_4)_2PbCl_6$ etc
Chlorite; chlorate; perchlorate		$Pb(ClO)_2$ , $Pb(ClO_3)_2$ , $Pb(ClO_4)_2$	—
Bromides		$PbBr_2$ , double and basic salts	$(C_2H_5NH_4)_2PbBr_4$
Iodides		$PbI_2$ , double and basic salts	$(C_2H_5NH_4)_2PbI_4$
Iodate, periodate		$Pb(IO_3)_2$ , several periodates	—
Oxides	$Pb_2O$	$PbO$	$PbO_2$
Hydroxides		$Pb(OH)_2$	$H_2PbO_4$ , $H_4Pb(OH)_6$
Salts		$HPhOONa$ in solution	$Pb_2PbO_4$ , $K_2PbO_4$ , $Pb_2PbO_4$ , $Ca_2PbO_4$
Sulphide		$PbS$ sulphohalides poly sulphide	—
Sulphite		$PbSO_3$	$Pb(SO_4)_2$
Sulphates		$PbSO_4$ various basic salts	—
Persulphate		$PbS_2O_8$	—
Thiosulphate		$PbS_2O_3$	—
Dithionate		$PbS_2O_6$	—
Selenide, selenite, selenate		$PbSe$ , $PbSeO_3$ , $PbSeO_4$	—
Telluride, tellurite, tellurate		$PbTe$ , $PbTeO_3$ , $PbTeO_4$	—
Azide, azide		$Pb(N_3)_2$ , $PbNH$	—
Hyponitrite, nitrite		$Pb(NO)_2$ , $Pb(NO_2)_2$ , basic salts	—
Nitrate		$Pb(NO_3)_2$ , basic salt	—
Phosphide, hypophosphite, phosphite		$Pb_3P$ , $Pb_3H$ , $Pb_3O_3$ , $PbHPO_3$	—
Phosphates		$Pb_3(PO_4)_2$ , acid, basic and double salts, $Pb_2P_2O_7$ , $Pb_2P_2O_6$	—
Arsenite, arsenates		$Pb_3(AsO_3)_2$ , $Pb_3AsO_4$ , $Pb_3AsO_5$	—
Metantimonate		$Pb(SbO_3)_2 \cdot 9H_2O$	—
Carbonate		$PbCO_3$ , $2PbCO_3 \cdot Pb(OH)_2$ , other basic salts	—
Formate		$Pb(COO)_2$	—
Acetate, etc		$Pb(C_2H_3O_2)_2 \cdot 3H_2O$ basic and complex salts, $PbC_2O_4$	$Pb(C_2H_3O_2)_4$ other organic salts
Oxalate		$PbC_2O_4$	—
Tartrate		$PbC_4H_4O_6$	—
Silicates		$Pb_2SiO_4$ , $PbSiO_3$ etc,	—
Borate		$Pb(BO_3)_2$ etc	—
Chromates		$PbCrO_4$ , $PbCr_2O_7$ , basic salts	—

## LEAD ALKYLs

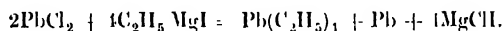
Lead, like tin, forms no hydride. It resembles the other metals of Subgroup IV B in forming volatile alkyls in which the metal is quadrivalent. The formation of these compounds by the interaction of zinc alkyls and lead dichloride with the separation of metallic lead emphasises the non-existence of lead dialkyls.

**Lead Tetramethyl** (*Tetramethide*),  $\text{Pb}(\text{CH}_3)_4$ , formed<sup>1</sup> from lead chloride and zinc methyl thus:



or from lead-sodium alloy and methyl iodide, is a liquid boiling at  $110^\circ \text{C}$ . and having a density of 2.034 at  $0^\circ \text{C}$ . The halides  $\text{Pb}(\text{CH}_3)_3\text{Cl}$ ,  $\text{Pb}(\text{CH}_3)_3\text{Br}$ ,  $\text{Pb}(\text{CH}_3)_3\text{I}$  result from action of the corresponding halogens on the tetramethyl, and are crystalline solids easily soluble in alcohol.

**Lead Tetraethyl** (*Tetraethide*),  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , is obtained from lead chloride and zinc methyl,<sup>2</sup> or by means of the Gignard reaction,<sup>3</sup> thus:



This compound is a liquid which cannot be distilled under ordinary pressure without decomposition, but boils at  $152^\circ \text{C}$ . under 190 mm. pressure. It has a density of 1.62. The lowering of freezing-point of ethylene bromide by lead tetraethyl has been determined by Ghira.<sup>4</sup>

The chloride<sup>5</sup>  $\text{Pb}(\text{C}_2\text{H}_5)_3\text{Cl}$ , formed by the action of hydrogen chloride on the tetraethyl, crystallises in needles; and the iodide results from the action of iodine on the same compound, and of magnesium ethyl iodide on lead chloride.<sup>6</sup> These halides are salts, derived from the base<sup>6</sup>  $\text{Pb}(\text{C}_2\text{H}_5)_3\text{OH}$ , which is formed by treating the iodide with moist silver oxide or distilling the chloride with potash. This base crystallises in needles, which are slightly soluble in water, have a strongly alkaline reaction, absorb carbon dioxide from the air, and combine with acids to form crystalline salts; e.g. the sulphate  $[\text{Pb}(\text{C}_2\text{H}_5)_3]_2\text{SO}_4$ , which is slightly soluble in water.

**Lead Triethyl**,  $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ , described by Lowig and by Klippel,<sup>7</sup> probably does not exist.<sup>8</sup>

**Lead Tetraphenyl**,  $\text{Pb}(\text{C}_6\text{H}_5)_4$ , is formed by heating brombenzene, in ethylacetate solution, with lead-sodium alloy,<sup>7</sup> or by the Gignard reaction,<sup>3</sup> i.e. by the action of lead chloride on an ethereal solution of magnesium phenyl bromide. This reaction serves to separate lead from radium-D.<sup>8</sup> Lead tetraphenyl crystallises in needles which melt at  $224^\circ$ – $225^\circ \text{C}$ ., and is converted by boiling nitric acid into lead diphenyl nitrate,  $(\text{C}_6\text{H}_5)_2\text{Pb}(\text{NO}_3)_2$ , whence other salts can be prepared.

<sup>1</sup> Cahours, *Ann. Chim.*, 1862, 122, 67; *Jahresber.*, 1861, 552.

<sup>2</sup> Buckton, *Ann. Chim.*, 1859, 112, 226; Frankland and Lawrance, *Trans. Chem. Soc.*, 1879, 35, 245.

<sup>3</sup> Pfeiffer and Trusker, *Ber.*, 1901, 37, 1125.

<sup>4</sup> Ghira, *Gazzetta*, 1891, 24, 1, 309.

<sup>5</sup> Lowig, *Ann. Chim.*, 1853, 88, 318; Klippel, *Jahresber.*, 1860, 380.

<sup>6</sup> Ghira, *Gazzetta*, 1894, 24, 1, 42.

<sup>7</sup> Polis, *Ber.*, 1887, 20, 717, 3331; Werner and Pfeiffer, *Zeitsch. anorg. Chem.*, 1898, 17, 100.

<sup>8</sup> Hofmann and Wolff, *Ber.*, 1907, 40, 2425.

Lead tetra-*p*-tolyl and the corresponding di-*p*-tolyl salts also exist.<sup>1</sup>

**Lead Ethoxide,**<sup>2</sup>  $\text{Pb}(\text{OC}_2\text{H}_5)_2$ , is obtained when lead in thin sheets is suspended over absolute ethyl alcohol through which ozone is passed. After washing with alcohol, and drying over sulphuric acid *in vacuo*, it forms a light yellow powder, which is soluble in water, but is readily hydrolysed. Several other lead alkyl oxides have been prepared.<sup>3</sup>

#### LEAD AND THE HALOGENS

**Lead Fluorides.** Lead forms a di- and a tetra-fluoride, and the latter gives rise to complex salts.

**Lead Fluoride,**  $\text{PbF}_2$ , is obtained as a white solid by the action of aqueous hydrofluoric acid on litharge or lead carbonate, or by precipitating the solution of a lead salt with a soluble fluoride. The heat of formation of this compound by the reaction  $\text{Pb}(\text{OH})_2 + 2\text{HF}$  (gas) is 18,600 calories<sup>4</sup>; it is easily fused to a yellow liquid, and has a density of 8.211. It is almost insoluble in water and aqueous hydrofluoric acid, but easily dissolves in hydrochloric and nitric acids. Its solubility in water at 18° C. has been deduced by Kohlrausch<sup>5</sup> from the conductivity of its saturated solution. The specific conductivity of the salt is 131, and 1 litre of a saturated solution contains 610 milligrams. Although an aqueous solution of lead fluoride shows little evidence of hydrolysis, the solid salt is hydrolysed by water-vapour into hydrofluoric acid and a basic salt.<sup>6</sup>

A *chlorofluoride* of lead,  $\text{PbFCl}$  or  $\text{PbF}_2 \cdot \text{PbCl}_2$ , was prepared by Berzelius by precipitating a solution of sodium fluoride with lead chloride. It may also be obtained from lead fluoride and ammonium chloride,<sup>7</sup> and crystallises in quadratic plates. It is slightly soluble in water without decomposition. Various double salts of lead fluoride with other halides of the same metal have been prepared by Sandommi.<sup>8</sup>

**Lead Tetrafluoride,**  $\text{PbF}_4$ , was prepared by Brauner,<sup>9</sup> in an impure state, by adding potassium hydrogen plumbifluoride,  $\text{K}_2\text{HPbF}_6$ , to cold concentrated sulphuric acid. Hydrogen fluoride gas escapes, whilst a yellow solution is formed, and then a penetrating vapour is evolved which is thought to be lead tetrafluoride. Gradually, however, the liquid becomes gelatinous, and then probably contains the tetrafluoride in a colloidal state, whilst heating it to 100–110° C. causes a yellow powder to separate, which is believed to be a third modification of the tetrafluoride, since it liberates iodine from potassium iodide solution, gives lead dioxide with water, and dissolves in hydrofluoric acid forming hydrofluoplumbic acid.

**Hydrofluoplumbic Acid,**  $\text{H}_2\text{PbF}_6$ , is probably formed in solution when lead tetra acetate is dissolved in concentrated hydrofluoric acid. When this solution is evaporated, lead dioxide separates (Brauner).

The potassium salt  $\text{K}_2\text{HPbF}_6$  was prepared by Brauner<sup>9</sup> by acting

<sup>1</sup> Polz, *Ber.*, 1888, 21, 3125.

<sup>2</sup> F. M. Parkin, *Proc. Chem. Soc.*, 1908, 179.

<sup>3</sup> Chablay, *Compt. rend.*, 1911, 153, 904.

<sup>4</sup> Gindz, *Ann. Chem. Phys.*, 1881 [iv], 3, 41.

<sup>5</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1901, 50, 355.

<sup>6</sup> Kohlrausch, *ibid.*, 1908, 64, 129.

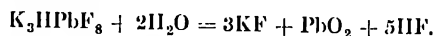
<sup>7</sup> Fenzles-Diacon, *Bull. Soc. chim.*, 1897, [iii], 17, 346.

<sup>8</sup> Sandommi, *Atti R. Acad. Lincei*, 1911, [v], 20, 1, 172, 253.

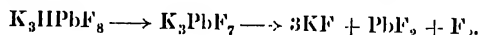
<sup>9</sup> Brauner, *Trans. Chem. Soc.*, 1894, 65, 393.



on the freshly precipitated oxide  $\text{Pb}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$  with a solution of potassium hydrogen fluoride in aqueous hydrofluoric acid, by fusing together lead dioxide and potassium fluoride and mixing hydrofluoric acid with the product, and by bringing together lead tetra-acetate potassium hydrogen fluoride and hydrofluoric acid. The solution obtained in either of these ways is evaporated in a vacuum desiccator, when monochmic needles of the required salt are obtained. These are isomorphous with the corresponding tin salt  $\text{K}_3\text{HSnF}_6$ . The salt is stable in dry air,<sup>1</sup> but is decomposed by water with separation of hydrogen fluoride, thus:



At  $230^\circ \text{C}$ . hydrogen fluoride is evolved, and at a higher temperature fluorine, thus:



It is noteworthy that this reaction furnishes a chemical method of preparing fluorine.

**Lead Chlorides** Lead forms a di- and a tetra-chloride, and each of these forms double or complex salts.

**Lead Chloride**,  $\text{PbCl}_2$ , occurs as the somewhat rare mineral *cotunnite*, which is of volcanic origin, and has been found in the crater and lava of Vesuvius. It was known to Dioscorides that yellow oxide of lead turns white when placed in warm water with common salt.

Lead chloride may be obtained in various ways. Chlorine slowly attacks lead, forming the chloride; the metal dissolves in dilute hydrochloric acid in presence of air, but in the strong acid, with evolution of hydrogen, to form the chloride; also the oxide, hydroxide, or carbonate may be dissolved in hydrochloric acid; but a more usual way of preparing this salt is to precipitate a moderately concentrated solution of the nitrate or acetate with hydrochloric acid or a soluble chloride. The chloride may then be purified by recrystallisation from hot water.

Lead chloride crystallises anhydrous in white, silky, rhombic needles, having a density of 5.802. Numerous observers<sup>2</sup> have determined the melting-point of this salt, which lies between  $485^\circ \text{C}$ . and  $512^\circ \text{C}$ . Its boiling-point is  $956^\circ \text{C}$ ., and its vapour has a density of 9.64 (air = 1) or 138.8 (H = 1) at  $1070^\circ \text{C}$ ., which corresponds to the molecular formula  $\text{PbCl}_2$ .<sup>3</sup> In the fused state molecular association exists.<sup>4</sup> The specific heat of the solid salt between ordinary temperature and  $100^\circ \text{C}$ . was found by Regnault<sup>5</sup> to be 0.0664, and its molecular heat of formation is 82,800<sup>6</sup> or 83,900<sup>7</sup> calories, or, according to Koref and Braune, 85,570 calories.<sup>8</sup>

<sup>1</sup> Ruff, *Zeitsch. angew. Chem.*, 1907, 20, 1217.

<sup>2</sup> Carnelley, *J. Chem. Soc.*, 1876, 29, 489; Weber, *Zeitsch. anorg. Chem.*, 1899, 21, 305; Ehrhardt, *Ann. Physik*, N.F., 1885, 24, 215; Lorenz and Ruckstuhl, *Zeitsch. anorg. Chem.*, 1906, 51, 71; Lorenz, Frei, and Jabs, *Zeitsch. physikal. Chem.*, 1904, 61, 468; Ruer, *Zeitsch. anorg. Chem.*, 1906, 49, 365; Goodwin and Kalmus, *Phys. Review*, 1909, 28, 1; Mönckmeyer, *Zeitsch. Kristallogr.*, 1908, 45, 609.

<sup>3</sup> Roscoe, *Proc. Roy. Soc.*, 1878, 27, 428; Scott, *Proc. Roy. Soc. Edin.*, 1887, 410.

<sup>4</sup> Lorenz, Kauffler, and Liebmann, *Ber.*, 1908, 41, 3727.

<sup>5</sup> Regnault, *Ann. Chim.*, 1841, [iii], 1, 129.

<sup>6</sup> Thomsen, *J. prakt. Chem.*, 1872, [ii], 12, 92.

<sup>7</sup> Berthelot, *Thermochimie*, 1897, 1, 338.

<sup>8</sup> Koref and Braune, *Zeitsch. Elektrochem.*, 1912, 18, 818.

## LEAD AND ITS COMPOUNDS

Lead chloride is sparingly soluble in cold and considerably more soluble in hot water. The solubility of lead chloride in water is as follows 1:

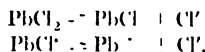
Temp °C	0°	15°	25°	35°	55°	80°	95°
Grams of $PbCl_2$ in 100 grams $H_2O$	0.6728	0.9090	1.0812	1.3214	1.8263	2.6224	3.1654

These data have a twofold bearing in qualitative analysis, for thence it follows that lead is but partially precipitated from solution by dilute hydrochloric acid, but that this substance can be identified by its crystallisation from boiling water, from which it separates in white, shining needles. This salt is less soluble in dilute solutions of hydrochloric acid and other chlorides, but more soluble in concentrated hydrochloric acid solution than in water. Thus its solubility varies in the following manner with the strength of the hydrochloric acid 2:

Grams HCl per litre	0	1	10	100	200	250	300	400
Grams $PbCl_2$ per litre								
(i) at 0° C.	5.83	3.6	1.2	1.2	5.2	10.5	17.5	40.0
(ii) at 25° C.	10.79	7.6	1.8					

In consequence of these facts a concentrated hydrochloric acid solution of lead chloride is precipitated by water, and an aqueous solution by a little hydrochloric acid. The ionic theory affords a satisfactory explanation of these solubilities. First, the addition of a little hydrochloric acid to the saturated aqueous solution increases the concentration of the chloride ions so that the solubility product of lead chloride is exceeded and precipitation takes place. Secondly, the presence of much hydrochloric acid promotes the formation of complex ions, so that more lead chloride dissolves. The fact that a concentrated hydrochloric acid solution is not precipitated by hydrogen sulphide is attributed to the lead being present in the form of a complex ion.

The state of ionisation of lead chloride in aqueous solution has been investigated by Noyes,<sup>3</sup> Feinman,<sup>4</sup> and von Ende.<sup>5</sup> Contrary to the opinions of the two former observers, the latter has concluded that this salt is ionised in two stages, thus



and has estimated the condition of a saturated solution at 25.2° C., which is 0.0388 normal, to be as follows

Undissociated $PbCl_2$	6.2 per cent.
$Pb^{++}$ ions	50.1 " "
$PbCl$ ions	13.7 " "

The following results have been obtained by Bottger<sup>6</sup> for the ionic concentration in equivalents per litre of a saturated solution of

<sup>1</sup> Taken from Seidell, *Solubilities of Inorganic and Organic Substances* (Crosby Lockwood, 1911).

<sup>2</sup> Dutte, *Compt. rend.*, 1881, 92, 718.

<sup>3</sup> Noyes, *Zeitsch. physikal. Chem.*, 1892, 7, 603.

<sup>4</sup> Feinman, *Zeitsch. anorg. Chem.*, 1898, 17, 327.

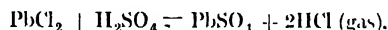
<sup>5</sup> Von Ende, *Zeitsch. anorg. Chem.*, 1903, 26, 162, see also Bottger, *Zeitsch. physikal. Chem.*, 1903, 46, 372.

<sup>6</sup> Bottger, *Zeitsch. physikal. Chem.*, 1903, 46, 602.

lead chloride at 19.95° C. :  $\text{Pb}^{++}$  0.0168;  $\text{PbCl}^+$  0.0109;  $\text{Cl}^-$  0.0444; and undissociated  $\text{PbCl}_2$  0.00127.

Lead chloride solution is hydrolysed to a very small extent; Ley found,<sup>1</sup> by its power of inverting cane-sugar, that a 0.01 normal solution of this salt is hydrolysed to the extent of 0.6 per cent. at 100° C.

Lead chloride may be distilled in an atmosphere of carbon dioxide,<sup>2</sup> but it is reduced by hydrogen below its melting-point, and decomposed by water-vapour at 110° C. and above into a basic chloride and hydrogen chloride gas. The reaction between lead chloride and anhydrous sulphuric acid,



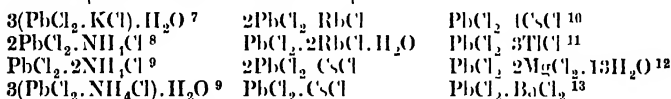
has been studied by Schreinemakers,<sup>3</sup> who finds the pressure of hydrogen chloride gas evolved reaches 1 atmosphere at 27.2° C.

**Lead Chloride Double Salts.** The solubility of lead chloride in water is diminished by the presence of small quantities of potassium chloride, and increased when the concentration of the latter salt passes a certain value. The minimum solubility of lead chloride at 25° C. is 0.00183 gram-molecule per litre, and is reached when the potassium chloride is of 1.5018 N strength.<sup>4</sup>

This variation in solubility, which is similar to that of lead chloride in hydrochloric acid, is attributed to the same cause, viz. to the mass action of chloride ions at low concentration, and to the formation of complex ions  $\text{PbCl}_4^{--}$  at higher concentrations.

The existence of several double chlorides of lead and potassium has been shown by Lorenz and Ruckstuhl,<sup>5</sup> who have examined the freezing-point curve of a fused mixture of the two salts. Thus by a maximum at 130° C. and 33.3 mol per cent of potassium chloride, and breaks at 140° C. and 180° C. with 60 mol and 68 mol per cent, respectively of potassium chloride, the existence of the following double salts is indicated:  $2\text{PbCl}_2 \cdot \text{KCl}$ , which forms an almost transparent, glassy mass;  $\text{PbCl}_2 \cdot 2\text{KCl}$ , which occurs in rhombic crystals; and  $\text{PbCl}_2 \cdot 4\text{KCl}$ , which is said to form reddish white, granular masses. The behaviour of a fused mixture of potassium and lead chlorides on electrolysis shows that a complex anion is present.<sup>6</sup>

The following crystallised double chlorides have been obtained from mixed aqueous solutions of their component salts:



<sup>1</sup> Ley, *Zeitsch. physikal. Chem.*, 1899, 30, 193.

<sup>2</sup> Benrath, *Zeitsch. physikal. Chem.*, 1908, 64, 693.

<sup>3</sup> Schreinemakers, *Chem. Weekblad*, 1904, 1, 87.

<sup>4</sup> Von Ende, *Zeitsch. anorg. Chem.*, 1901, 25, 129.

<sup>5</sup> Lorenz and Ruckstuhl, *Zeitsch. anorg. Chem.*, 1906, 51, 71.

<sup>6</sup> Lorenz and Fausti, *Zeitsch. Elektrochem.*, 1904, 10, 633.

<sup>7</sup> Wells, *Zeitsch. anorg. Chem.*, 1893, 3, 195; Remsen and Herty, *Amer. Chem. J.*, 1892, 14, 81, 107.

<sup>8</sup> Andrieu, *Compt. rend.*, 1884, 96, 135, 1502; Fonzees-Duacou, *Bull. Soc. chim.*, 1897, [iii], 17, 316; Randall, *Amer. Chem. J.*, 1893, 15, 191.

<sup>9</sup> Wells and Johnson, *Zeitsch. anorg. Chem.*, 1893, 4, 117; Demasseux, *Compt. rend.*, 1913, 156, 892.

<sup>10</sup> Wells, *Zeitsch. anorg. Chem.*, 1893, 3, 195; 4, 128.

<sup>11</sup> Noyes, *Zeitsch. physikal. Chem.*, 1892, 9, 603.

<sup>12</sup> Otto and Drewes, *Arch. Pharm.*, 1890, 228, 495.

<sup>13</sup> Becquerel, *Compt. rend.*, 1852, 34, 29.

## LEAD AND ITS COMPOUNDS

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According to Foote and Levy,<sup>1</sup> only one lead ammonium chloride, viz.,  $2\text{PbCl}_2 \cdot \text{NH}_4\text{Cl}$ , exists. Equilibria in the system water-ammonium chloride-lead chloride have been studied by Brønsted.<sup>2</sup>

Two compounds of lead chloride with ammonium bromide have been described<sup>3</sup>; they are  $2\text{PbCl}_2 \cdot \text{NH}_4\text{Br}$  and  $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Br}$ . Lead chloride forms with pyridine the substance  $\text{PbCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , which crystallises in needles, and rapidly loses pyridine in the air.<sup>4</sup>

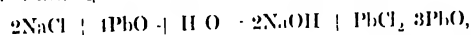
**Basic Lead Chlorides.** Various basic lead chlorides exist. Owing to the tendency of lead to form basic salts, basic chlorides are more common in nature than the normal salt. Thus the mineral *matlockite* is  $\text{PbCl}_2 \cdot \text{PbO}$ , and is formed artificially by heating the normal chloride in the air until no more fumes are evolved. The mineral *mundipite*  $\text{PbCl}_2 \cdot 2\text{PbO}$  is also well known. When lead chloride is fused with lead oxide a yellow product results, which is used as a pigment under the name *Cassel yellow*; it has approximately the composition  $\text{PbCl}_2 \cdot 7\text{PbO}$ , but is not a single substance. Various complex basic chlorides<sup>5</sup> are formed when chlorine and air act on litharge at high temperature; but they are probably mixtures. The basic lead chlorides have been investigated by Ruet,<sup>6</sup> who has traced the freezing-point curve of fused mixtures of lead oxide and lead chloride, and concludes that only the following three anhydrous basic chlorides exist:

(1)  $\text{PbCl}_2 \cdot \text{PbO}$ , which occurs naturally as *matlockite*. This compound crystallises in long, thin needles, and cannot be melted without decomposition, but decomposes at  $524^\circ \text{C}$ , yielding the second basic chloride.

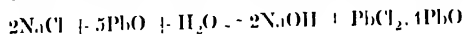
(2)  $\text{PbCl}_2 \cdot 2\text{PbO}$ , which exists naturally as *mundipite*, forms long, shining needles, that melt, undecomposed, at  $693^\circ \text{C}$ .

(3)  $\text{PbCl}_2 \cdot 4\text{PbO}$  has not been found in nature, but crystallises in yellow plates, and yields a bright yellow powder. It melts, unchanged, at  $711^\circ \text{C}$ .

Several hydrated basic lead chlorides, or lead hydroxychlorides, exist, among them being the mineral *laurentite*  $\text{PbCl}_2 \cdot \text{PbO} \cdot 4\text{H}_2\text{O}$  or  $\text{Pb}(\text{OH})\text{Cl}$ . An artificial form of this substance was at one time prepared by precipitating lead chloride solution with lime water. The process was patented by Pattinson in 1849, and the product used as a substitute for white lead. This compound, as well as  $\text{PbCl}_2 \cdot 3\text{PbO} \cdot 11\text{H}_2\text{O}$ , appears also to be formed when lead chloride is shaken with water and the hydrated oxide  $\text{Pb}_3\text{O}_4 \cdot 4\text{H}_2\text{O}$ .<sup>7</sup>  $\text{PbCl}_2 \cdot 3\text{PbO}$  is also supposed to be produced in Scheele's process for manufacturing caustic soda by the action of litharge on sodium chloride solution, thus



but according to Berl and Austerweil<sup>8</sup> the compound  $\text{PbCl}_2 \cdot 4\text{PbO} \cdot 2\text{H}_2\text{O}$  is produced when a normal solution of sodium chloride is employed, thus:



<sup>1</sup> Foote and Levy, *Trans. Chem. Soc.*, 1907, 34, 119.

<sup>2</sup> Brønsted, *Second Intern. Congr. Appl. Chem.*, 1909, 1, 110.

<sup>3</sup> Ponze, *Bull. Soc. Chim.*, 1897, [3] 17, 316.

<sup>4</sup> Heise, *J. Physiol. Chem.*, 1912, 16, 173.

<sup>5</sup> Cross and Segmüller, *J. Chem. Soc.*, 1878, 33, 105.

<sup>6</sup> Ruet, *Zetsch. anorg. Chem.*, 1906, 49, 365.

<sup>7</sup> Fleissner and Austerweil, *Abhandl. Kais. d. Ges. sandh. Forsch.*, 1907, 26, Heft 3.

<sup>8</sup> Berl and Austerweil, *Zetsch. Elektrochem.*, 1907, 13, 165.

The hydroxychloride formed in Scheele's process turns yellow when heated till it is anhydrous. In 1787 Turner took out a patent for preparing caustic soda by Scheele's reaction, and the ignited basic chloride was employed as a pigment under the name of *Turner's yellow*, or *patent yellow*.

Stromholm<sup>1</sup> has prepared the salt  $2\text{PbCl}_2 \cdot 6\text{PbO} \cdot 11\text{H}_2\text{O}$ , and finds that it crystallises in yellow needles; he has also obtained the salt  $\text{PbCl}_2 \cdot 6\text{PbO} \cdot 21\text{H}_2\text{O}$ , crystallised in needles which on heating change in colour from grey to yellow.

**Lead Tetrachloride,  $\text{PbCl}_4$ .**—Complex salts of the type  $\text{M}'_2\text{PbCl}_6$  were prepared before the tetrachloride itself was isolated. First it was observed that lead dioxide can be dissolved in cold concentrated hydrochloric acid without the evolution of chlorine<sup>2</sup>; also that a solution of sodium chloride saturated with chlorine can dissolve a considerable quantity of lead dichloride,<sup>3</sup> and that hydrochloric acid itself may be employed in place of sodium chloride.<sup>4</sup> These facts indicate the probable existence in solution of complex ions containing quadrivalent lead; and the ammonium salt  $(\text{NH}_4)_2\text{PbCl}_6$  was obtained in an impure state from such solution by Nikoljukin.<sup>5</sup> The tetrachloride itself was first isolated by Friedrich,<sup>6</sup> who prepared ammonium plumbichloride by passing chlorine into hydrochloric acid containing lead dichloride in suspension, and then adding ammonium chloride to the liquid. When the separated ammonium complex salt was added to well-cooled sulphuric acid there was a vigorous reaction, with evolution of hydrogen chloride gas, and the separation of a yellow liquid, which was lead tetrachloride.

Lead tetrachloride is a yellow, mobile, refractive liquid, having a density of 3.18 at  $0^\circ \text{C}$ .; it solidifies at  $-15^\circ \text{C}$ . to a yellowish, crystalline mass. It is fairly stable under concentrated sulphuric acid, but fumes in moist air and decomposes into lead dichloride and chlorine; at  $105^\circ \text{C}$ . it decomposes explosively.

With a little water it forms an unstable hydrate, but with much water it is decomposed into lead dioxide and hydrochloric acid. With a little well-cooled, concentrated hydrochloric acid it yields yellow crystals which are probably *hydrochloroplumbic acid*,  $\text{H}_2\text{PbCl}_6$ . A yellow solution of this acid is obtained when concentrated hydrochloric acid is electrolysed with a lead anode.<sup>7</sup>

**Ammonium Plumbichloride,  $(\text{NH}_4)_2\text{PbCl}_6$ ,** has been prepared in several ways. It is obtained when cold hydrochloric acid acts on lead dioxide, and ammonium chloride is added to the resulting solution<sup>8</sup>; by treating lead dichloride with fuming hydrochloric acid and chlorine under pressure, and then adding ammonium chloride<sup>9</sup>; by adding ammonium chloride to the solution of hydrochloroplumbic acid obtained by electrolysis,<sup>7</sup> or to a solution of lead tetra-acetate in hydro-

<sup>1</sup> Stromholm, *Zeitsch anorg Chem*, 1901, 38, 429

<sup>2</sup> Millon, *Journ Pharm Chem*, 1842, [iv], 28, 299

<sup>3</sup> Sobrero and Selmi, *Jahresber*, 1850, 322

<sup>4</sup> Ditte, *Compt rend*, 1881, 91, 765.

<sup>5</sup> Nikoljukin, *J Russ Phys Chem Soc*, 1885, 207

<sup>6</sup> Friedrich, *Ber*, 1893, 26, 1434; see also Classen and Zahorski, *Zeitsch. anorg Chem.*, 1893, 4, 100

<sup>7</sup> Elbs and Nubling, *Zeitsch Elektrochem*, 1903, 9, 176

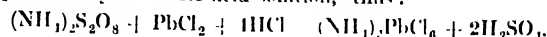
<sup>8</sup> Nikoljukin, *loc cit*.

<sup>9</sup> Classen and Zahorski, *Zeitsch anorg Chem*, 1893, 4, 100

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chloric acid<sup>1</sup>; and by the interaction of lead dichloride and ammonium persulphate in hydrochloric acid solution,<sup>2</sup> thus:



Ammonium plumbichloride crystallises in citron-yellow octahedra, isomorphous with  $(\text{NH}_4)_2\text{SnCl}_6$  and  $(\text{NH}_4)_2\text{PtCl}_6$ . It is stable in the air, and may be heated to 115° C. without perceptible decomposition; it decomposes,<sup>3</sup> however, at 225° C. This salt has been employed for chlorinating aromatic hydrocarbons and their derivatives.<sup>4</sup>

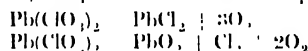
Potassium, rubidium, and caesium plumbichlorides resemble the ammonium salt;  $\text{K}_2\text{PbCl}_6$  decomposes at 190° C.,  $\text{Rb}_2\text{PbCl}_6$  and  $\text{Cs}_2\text{PbCl}_6$  at about 280° C.<sup>5</sup> The quinoline and pyridine salts,  $(\text{C}_9\text{H}_7\text{NH})_2\text{PbCl}_6$  and  $(\text{C}_5\text{H}_5\text{NH})_2\text{PbCl}_6$ , respectively, have been prepared.<sup>6</sup>

A number of plumbichlorides have been prepared by Gutbier and Wissmüller<sup>6</sup> by mixing hydrochloroplumbic acid with solutions of metallic or substituted ammonium chloride. These salts are anhydrous, being  $\text{X}_2\text{PbCl}_6$  or  $(\text{R} \cdot \text{NH}_4)_2\text{PbCl}_6$ , and are obtained in minute yellow or red crystals. Compounds of the alkali metals and derivatives of the pyridine and quinoline series, are stable; aliphatic ammonium compounds tend to decompose in the air, evolving chlorine.

Lead tetrachloride forms compounds with ammonia and organic bases.<sup>7</sup>

**Lead Chlorite**,  $\text{Pb}(\text{ClO}_2)_2$ , is obtained by precipitating lead nitrate solution with a soluble chlorite.<sup>8</sup> It crystallises in yellow scales, and explodes when heated above 100° C. A mixture of this salt with sulphur inflames when rubbed.

**Lead Chlorate**,  $\text{Pb}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ , is obtained by adding lead oxide or carbonate in excess to chloric acid solution, allowing the solution to stand for a day, and then filtering and concentrating the filtrate. The crystals are monoclinic,<sup>9</sup> and are isomorphous with those of the corresponding barium salt,  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ . The salt may be dehydrated by heating under greatly reduced pressure to 130–140° C. The manner of decomposition of anhydrous lead chlorate by heat is interesting because it may be compared with the Linné decomposition of potassium chlorate. The subject has been investigated by Sodemann,<sup>10</sup> who has shown that chlorine is evolved together with oxygen, and that in the slow decomposition of the salt under 4 mm. pressure at 225°–260° C. the following independent reactions take place:



and that lead peroxide and chlorine interact thus:



<sup>1</sup> Hutchinson and Pollard, *Trans. Chem. Soc.*, 1896, 66, 212.

<sup>2</sup> Seyewitz and Tiawitz, *Compt. rend.*, 1903, 136, 686.

<sup>3</sup> Wells, *Zeitsch. anorg. Chem.*, 1893, 4, 335.

<sup>4</sup> Seyewitz and Biel, *Compt. rend.*, 1902, 135, 1120. Seyewitz and Tiawitz, *Compt. rend.*, 1903, 136, 240.

<sup>5</sup> Elbs and Nubling, *Zeitsch. Elektrochem.*, 1903, 9, 776. Claisen and Zdanowski, *Zeitsch. anorg. Chem.*, 1893, 4, 109.

<sup>6</sup> Gutbier and Wissmüller, *Lehrb. Chem.*, 1914, [n], 99, 191.

<sup>7</sup> Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 815.

<sup>8</sup> Schulz, *Ann. Chem.*, 1859, 109, 317. Millon, *Ann. Chim. Phys.*, 1842, [n], 7, 327.

<sup>9</sup> Marignac, *Jahresber.*, 1855, 398.

<sup>10</sup> Sodemann, *Trans. Chem. Soc.*, 1900, 77, 717.

so that the amount of chlorine actually evolved is much reduced. If the decomposition takes place rapidly at high temperature, the oxychloride  $\text{PbO} \cdot \text{PbCl}_2$  is formed.

The difference between the behaviour of lead and potassium chlorates when heated lies in the loss of chlorine by the former salt; and this difference may be attributed to the weaker basic nature of lead oxide. It may be suggested that the nitrates show a somewhat similar difference when heated, potassium nitrate retaining all its nitrogen as nitrate, whilst lead nitrate loses it all as  $\text{NO}_2$ , and is converted into oxide.

**Lead Perchlorate**,  $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , is formed, not by ignition of the chlorate, but by dissolving lead oxide or carbonate in aqueous perchloric acid. It crystallises in soluble, white needles, which hold their water very tenaciously. The basic salt  $\text{Pb}(\text{ClO}_4)_2 \cdot \text{PbO} \cdot 2\text{H}_2\text{O}$  is known.<sup>1</sup>

**Lead Bromides.** Only the dibromide of lead is definitely known, and this forms various double salts; derivatives of the tetrabromide have, however, been prepared.

**Lead Dibromide**,  $\text{PbBr}_2$ , resembles the corresponding chloride, and is prepared by dissolving lead oxide in hydrobromic acid and crystallising the solution, or by precipitating a lead salt with potassium bromide solution. It crystallises from hot water in white needles, which belong to the rhombic system, and have a density of 6.63.

If hydrobromic acid solution is added in excess to a 0.5 per cent. solution of lead bromide in hot water, needle-shaped crystals separate on cooling, which have the composition  $\text{PbBr}_2 \cdot 3\text{H}_2\text{O}$ .<sup>2</sup>

Various observations<sup>3</sup> have been made upon the melting-point of this salt, which lies between  $180^\circ \text{C}$ . and  $499^\circ \text{C}$ . When fused it is a red liquid, solidifying to a white, horny mass; if, however, it is melted in moist air it emits white fumes and forms an oxybromide. The boiling-point<sup>4</sup> of lead bromide is about  $920^\circ \text{C}$ ., and its molecular heat of formation from the metal and liquid bromine is 75,000 calories (Berthelot), or 64,450 calories (Thomsen<sup>5</sup>). This salt slowly darkens in the light owing to the separation of metal.<sup>6</sup>

The solubility of lead bromide in water increases rapidly with rising temperature as the following figures show<sup>7</sup>.

Temp. $^\circ \text{C}$	0	15	25	35	45	55	65	80	100
Grams $\text{PbBr}_2$ in 100 grams $\text{H}_2\text{O}$	0.4554	0.7305	0.9744	1.3220	1.7457	2.1376	2.574	3.343	4.751

According to von Ende,<sup>8</sup> the solubility at  $25.2^\circ \text{C}$ . is 0.02628 gram-

<sup>1</sup> Marignac, *Jahresber.*, 1855, 398; Serullas, *Ann. Chim. Phys.*, 1831, 46, 306; Roseoe, *Annalen*, 1862, 121, 356.

<sup>2</sup> Ditté, *Compt. rend.*, 1881, 92, 718.

<sup>3</sup> Euhardt ( $490^\circ \text{C}$ ), *Ann. Phys.*, N F, 1885, 24, 215; O. H. Weber ( $490^\circ \text{C}$ ), *Zeitsch. anorg. Chem.*, 1899, 21, 305; Carnelley ( $499^\circ \text{C}$ ) *J. Chem. Soc.*, 1878, 33, 273; Helfenstein ( $480^\circ \text{C}$ ), *Zeitsch. anorg. Chem.*, 1900, 23, 255; Goodwin and Kilbuck (1886 $^\circ \text{C}$ ), *Phys. Review*, 1909, 28, 1.

<sup>4</sup> Weber ( $918^\circ$   $920^\circ \text{C}$ ), *Zeitsch. anorg. Chem.*, 1899, 21, 305; Helfenstein ( $921^\circ \text{C}$ ), *Zeitsch. anorg. Chem.*, 1900, 23, 255.

<sup>5</sup> Thomsen, *J. prakt. Chem.*, 1875, [ii], 12, 92.

<sup>6</sup> Norris, *Ann. Chem.*, 1861, 117, 189.

<sup>7</sup> Lichty, *Amer. Chem. J.*, 1903, 25, 469.

<sup>8</sup> Von Ende, *Zeitsch. anorg. Chem.*, 1901, 26, 129.

molecule per litre, whilst the state of ionisation of the solution is as follows:

0.00106	gram-molecule of $\text{PbBr}_2$ (undissociated) per litre
0.00919	" $\text{PbBr}$ "
0.01603	" $\text{Pb}$ "
0.01125	" $\text{Br}'$ "

The following results have, however, been obtained by Bottger,<sup>1</sup> expressed in equivalents per litre:  $\text{PbBr}_2$  0.00111,  $\text{PbBr}$  0.0110,  $\text{Pb}$  0.0106,  $\text{Br}'$  0.0322.

In general, the solubility of lead bromide in hydrochloric, nitric, and acetic acids, as well as in ammonium chloride solution, is greater than in water; but the solubility of this compound in hydrogen bromide solution is analogous to that of lead chloride in hydrochloric acid, that is to say it is less soluble in dilute hydrogen bromide solution than in pure water: 1 litre of 0.5 normal solution of  $\text{HBr}$  dissolves only 1.25 gram  $\text{PbBr}_2$  at  $11^\circ\text{C}$ , whilst a litre of water at the same temperature dissolves 6 grains;<sup>2</sup> but more soluble in a concentrated solution than in pure water, owing to the formation of complex ions.<sup>3</sup>

**Double Salts of Lead Bromide.** Lead bromide forms a number of double salts with the bromides of more electropositive metals, and combines also with hydrobromic acid to form the crystalline complex acid  $2\text{HBr} \cdot 5\text{PbBr}_2 \cdot 10\text{H}_2\text{O}$ .<sup>4</sup> The following salts have been described:

$\text{PbBr}_2 \cdot 2\text{KBr}$ , <sup>5</sup>	$\text{PbBr}_2 \cdot 2\text{NH}_4\text{Br} \cdot \text{H}_2\text{O}$	$\text{PbBr}_2 \cdot 2\text{RbBr} \cdot \text{H}_2\text{O}$
$\text{PbBr}_2 \cdot 2\text{KBr} \cdot \text{H}_2\text{O}$ , <sup>5</sup>	$2\text{PbBr}_2 \cdot \text{NH}_4\text{Br}$ , <sup>6</sup>	and $2\text{PbBr}_2 \cdot \text{RbBr}$ , <sup>8</sup>
$3\text{PbBr}_2 \cdot 3\text{KBr} \cdot \text{H}_2\text{O}$ (?),	$\text{NH}_4\text{Pb}_2\text{Cl}_4\text{Br}$ ,	$\text{PbBr}_2 \cdot 4\text{CsBr}$ ,
$\text{PbBr}_2 \cdot 4\text{KBr} \cdot \text{H}_2\text{O}$ ,	$(\text{NH}_4)_2\text{Pb}_2\text{Br}_4\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	$\text{PbBr}_2 \cdot \text{CSbBr}$ ,
$2\text{PbBr}_2 \cdot \text{KBr}$	and $\text{NH}_4\text{Pb}_2\text{Br}_4\text{Cl}_2$ ,	$2\text{PbBr}_2 \cdot \text{CSbBr}$ , <sup>9</sup>
	$\text{PbBr}_2 \cdot 2\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ , <sup>10</sup>	

Compounds of lead chloride and bromide have been described<sup>11</sup>;  $\text{PbCl}_2 \cdot \text{PbBr}_2$  and  $3\text{PbCl} \cdot \text{PbBr}_2$ , but these may be isomorphous mixtures of the two salts.<sup>12</sup>

**Basic Lead Bromides.** When lead bromide is fused in moist air it is converted into a pearly yellow mass which is said to be  $\text{PbBr}_2 \cdot \text{PbO}$ , the hydrated salt  $\text{PbBr} \cdot \text{PbO} \cdot \text{H}_2\text{O}$  is obtained when sodium bromide and lead acetate solutions are heated together,<sup>13</sup> and also when lead bromide solution is treated with ammonia;

<sup>1</sup> Bottger, *Zeitsch. physikal. Chem.*, 1903, 46, 602.

<sup>2</sup> Andie, *Compt. rend.*, 1855, 97, 1302.

<sup>3</sup> Ditté, *Compt. rend.*, 1881, 92, 718.

<sup>4</sup> Löwig, *Gmelin's Handbook*, 1850, v, 161.

<sup>5</sup> Remsen and Herby, *Amer. Chem. J.*, 1892, 14, 81, 107; Wells, *Zeitsch. anorg. Chem.*, 1893, 3, 195.

<sup>6</sup> Wells and Johnson, *Zeitsch. anorg. Chem.*, 1893, 4, 117.

<sup>7</sup> Fonze-Ducon, *Bull. Soc. chim.*, 1895, [iii], 17, 316.

<sup>8</sup> Wells, *Zeitsch. anorg. Chem.*, 1893, 4, 128.

<sup>9</sup> Wells and Walden, *Ann. N. Y. Sci. Coll.*, 1893, [iii], 15, 121; *Zeitsch. anorg. Chem.*, 1893, 3, 203; Foote, *Amer. Chem. J.*, 1905, 37, 124; Wells and Wheeler, *Zeitsch. anorg. Chem.*, 1895, 3, 201.

<sup>10</sup> Otto and Drewes, *Arch. Hygien.*, 1890, 228, 195.

<sup>11</sup> Thomas, *Compt. rend.*, 1899, 128, 1231 and 1319; Hoes, *Chem. News*, 1881, 43, 216.

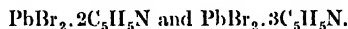
<sup>12</sup> Herby and Boggs, *J. Amer. Chem. Soc.*, 1897, 19, 820; Monkenmeyer, *Zeit. Krys. tallogr.*, 1908, 45, 609.

<sup>13</sup> De Schulten, *Bull. Soc. fran. Min.*, 1897, 20, 186.



the compound  $\text{PbBr}_2 \cdot 6\text{PbO} \cdot 2\text{H}_2\text{O}$  has also been obtained in white needles by the action of 0.05N KBr solution on lead hydroxide, whence  $4\text{PbBr}_2 \cdot 12\text{PbO} \cdot 8\text{H}_2\text{O}$  is formed in yellow microscopic needles by the action of caustic soda.<sup>1</sup> The compound  $\text{PbBr}_2 \cdot 2\text{PbO}$  is said also to exist.<sup>2</sup>

Lead bromide forms with pyridine the compounds<sup>3</sup>:



**Lead Tetrabromide** has never been prepared, but quinoline plumbibromide,  $(\text{C}_9\text{H}_7\text{NH})_2\text{PbBr}_6$ , is obtained when the corresponding chloride is decomposed by concentrated potassium bromide solution. That this is really a quadrivalent lead compound is shown by the fact that alkalis separate from it lead dioxide.<sup>4</sup>

**Lead Bromate**,  $\text{Pb}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ , crystallises from a hot solution of lead carbonate in bromic acid in shining monocline crystals, isomorphous with the corresponding strontium salt. Lead bromate is decomposed at  $180^\circ \text{C}$ . and leaves a residue of lead dioxide. One litre of a saturated solution at  $20^\circ \text{C}$ . contains 13.4 grams of the salt.

The basic salt  $\text{Pb}(\text{BrO}_3)_2 \cdot 3\text{PbO} \cdot 2\text{H}_2\text{O}$ <sup>5</sup> is obtained by the interaction of lead hydroxide and ammonium bromate solution.

**Lead Iodides.**—Lead forms only one iodide,  $\text{PbI}_2$ , which gives rise to double and basic salts; some derivatives of the unknown  $\text{PbI}_4$ , however, exist.

**Lead Iodide**,  $\text{PbI}_2$ , may be obtained by dissolving lead in hydriodic acid, or by precipitating a lead salt by means of a soluble iodide. When obtained in the latter way it is a bright yellow precipitate, which dissolves in much hot water and separates again on cooling in golden yellow six-sided plates. The density<sup>6</sup> of lead iodide is 6.16; when the dry salt is heated it becomes reddish yellow, then bright red and brownish black, and finally melts to a reddish brown liquid at about  $380^\circ \text{C}$ . Various estimations of the melting-point are as follow: Ramsay and Eumorfopoulos,<sup>7</sup>  $373^\circ \text{C}$ .; Ehrhardt,<sup>8</sup>  $375^\circ \text{C}$ .; Carnelley,<sup>9</sup> between  $374^\circ \text{C}$ . and  $387^\circ \text{C}$ ., with a mean value of  $383^\circ \text{C}$ . It boils<sup>10</sup> between  $861^\circ \text{C}$ . and  $954^\circ \text{C}$ ., and may be sublimed unchanged in an atmosphere of carbon dioxide.<sup>11</sup>

The molecular heat of formation of lead iodide from its elements is 89,800 calories<sup>12</sup>; or, according to Korf and Braune, 41,850 calories.<sup>13</sup>

Dry lead iodide is stable in the air; but the moist salt, under the influence of sunlight, yields lead carbonate and dioxide together with

<sup>1</sup> Stromholm, *Zeitsch. anorg. Chem.*, 1904, 38, 436.

<sup>2</sup> André, *Compt. rend.*, 1885, 97, 1302.

<sup>3</sup> Goebbels, *Ber.*, 1895, 28, 794; Heise, *J. Physical Chem.*, 1912, 16, 373.

<sup>4</sup> Classen and Zahorski, *Zeitsch. anorg. Chem.*, 1893, 4, 100; Elbs and Nubling, *Zeitsch. Elektrochem.*, 1903, 9, 776.

<sup>5</sup> Stromholm, *Zeitsch. anorg. Chem.*, 1904, 38, 429.

<sup>6</sup> Clarke, *Constants of Nature* (Washington, 1888), pt. 1.

<sup>7</sup> Ramsay and Eumorfopoulos, *Phil. Mag.*, 1896, 41, 360.

<sup>8</sup> Ehrhardt, *Ann. Physik*, N.F., 1885, 24, 215.

<sup>9</sup> Carnelley, *J. Chem. Soc.*, 1876, 29, 489.

<sup>10</sup> Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 126.

<sup>11</sup> Schtschorbakoff, *J. Russ. Phys. Chem. Soc.*, 1906, 37, 682.

<sup>12</sup> Thomsen, *J. prakt. Chem.*, 1875, [1], 12, 92.

<sup>13</sup> Korf and Braune, *Zeitsch. Elektrochem.*, 1912, 18, 818.

## LEAD AND ITS COMPOUNDS

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free iodine.<sup>1</sup> When the salt is heated in the air it loses iodine and forms an oxyiodide.

The solubility<sup>2</sup> of lead iodide in water is as follows:

Temp. °C	0	15	25	35	45	55	65	80	100
Grams $\text{PbI}_2$ in 100 grams $\text{H}_2\text{O}$	0.0142	0.0613	0.0761	0.1012	0.1133	0.1733	0.2183	0.3023	0.436

According to von Ende,<sup>3</sup> the solubility at 25 °C is 0.00158 gram-molecule per litre. This salt is thus much less soluble in water than the bromide or chloride. The solubilities of the three salts are shown in Fig. 15.

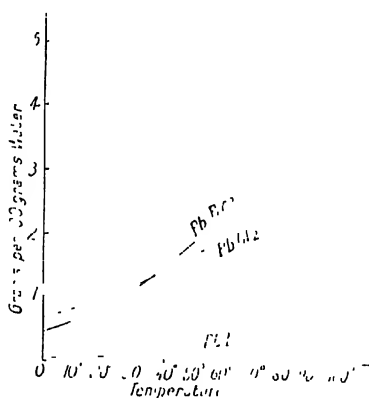


FIG. 15. Solubility curves of lead chloride, bromide, and iodide in water.

The solubilities of lead chloride, bromide, and iodide at 20 °C have been determined by Bottger<sup>4</sup> by comparing the electric conductivities of their saturated solutions with the conductivity of pure water. The following results were obtained:  $\text{PbCl}_2$   $9.61 \times 10^{-4}$ ,  $\text{PbBr}_2$   $8.34 \times 10^{-4}$ ,  $\text{PbI}_2$   $0.17 \times 10^{-4}$  grams per litre. Moreover, it was concluded that lead iodide is dissociated<sup>5</sup> only into  $\text{Pb}^{2+}$  and  $2\text{I}^-$  ions, no  $\text{PbI}^+$  ions being formed, the ion-concentration of this salt was  $2.53 \times 10^{-3}$  equivalents per litre, and the solubility product  $8.10 \times 10^{-9}$ .

An aqueous solution of lead iodide is colourless, the yellow colour being that of the solid salt, and not of  $\text{Pb}^{2+}$  or  $\text{I}^-$  ions. This salt is more soluble in alkali iodide and acetate solutions than in pure water, owing to the formation of complex ions. Indeed, lead iodide may be dissolved in concentrated potassium iodide solution and reprecipitated by dilution.

**Lead Iodide Double or Complex Salts.**—Lead iodide combines with hydriodic acid to form a crystalline compound, and with a large number of metallic iodides to form double salts.

<sup>1</sup> Schmidt, *Pogg. Annalen*, 1866, 127, 493.

<sup>2</sup> Lichty, *Am. Chem. J.*, 1903, 25, 469.

<sup>3</sup> Von Ende, *Zetsch. anorg. Chem.*, 1903, 26, 162.

<sup>4</sup> Bottger, *Zeitsch. physikal. Chem.*, 1903, 46, 602.

<sup>5</sup> See also von Ende, *Zetsch. anorg. Chem.*, 1903, 26, 159.

The compound  $\text{PbI}_2 \cdot 5\text{H}_2\text{O}$  is obtained in unstable crystals by the action of hydriodic acid on lead in presence of air, or by dissolving lead iodide in hydriodic acid<sup>1</sup>; and the following double iodides have been described:  $\text{PbI}_2 \cdot 2\text{LiI} \cdot 4\text{H}_2\text{O}$ ,<sup>2</sup>  $\text{PbI}_2 \cdot \text{LiI} \cdot 5\text{H}_2\text{O}$ ,<sup>3</sup>  $\text{PbI}_2 \cdot (\text{NaI})_2$ ,  $\text{PbI}_2 \cdot 2\text{NaI} \cdot 4\text{H}_2\text{O}$ ,<sup>2</sup>  $\text{PbI}_2 \cdot 2\text{NaI} \cdot 6\text{H}_2\text{O}$ ,<sup>2</sup>  $\text{PbI}_2 \cdot \text{KI} \cdot 2\text{H}_2\text{O}$ <sup>4</sup> (other potassium salts have been described,<sup>5</sup> but their existence is doubtful),  $3\text{PbI}_2 \cdot 4\text{NH}_4\text{I} \cdot 6\text{H}_2\text{O}$ ,<sup>2</sup>  $3\text{PbI}_2 \cdot 4\text{N}(\text{CH}_3)_3 \cdot \text{I}_2$ ,<sup>2</sup>  $\text{PbI}_2 \cdot \text{RbI} \cdot 2\text{H}_2\text{O}$ ,<sup>6</sup>  $\text{PbI}_2 \cdot \text{CsI}$ ; also double iodides containing the following elements:  $\text{Gl}$ ,  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Sn}''$ ,  $\text{Cr}''$ ,  $\text{Fe}''$ ,  $\text{Mn}''$ ,  $\text{Ni}''$ ,  $\text{Co}''$ ,  $\text{Al}$ ,  $\text{P}'''$ ,  $\text{As}'''$ ,  $\text{Sb}'''$ ,  $\text{Br}'''$ . The pyridine compounds  $\text{PbI}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$  and  $\text{PbI}_2 \cdot 3\text{C}_5\text{H}_5\text{N}$  have been prepared.<sup>8</sup>

The following chloriodides  $\text{PbI}_2 \cdot \text{PbCl}_2$  or  $\text{PbClI}$ <sup>9</sup> and  $3\text{PbClI} \cdot \text{H}_2\text{O}$ ,<sup>10</sup> and the bromiodide  $\text{PbI}_2 \cdot 3\text{PbBr}_2$  are said to exist, but it is questionable whether they are true compounds or isomorphous mixtures of the different halides.<sup>11</sup>

**Basic Lead Iodides.**—Various basic lead iodides have been described; they are formed by the action of potassium iodide solution on lead hydroxide, or of alkali hydroxide or ammonia on lead iodide:  $\text{PbI}_2 \cdot \text{PbO} \cdot \text{H}_2\text{O}$ ,<sup>12</sup>  $\text{PbI}_2 \cdot 2\text{PbO}$ ,  $\text{PbI}_2 \cdot \text{PbO} \cdot 2\text{H}_2\text{O}$ ,<sup>11</sup>  $\text{PbI}_2 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$ ,<sup>12</sup>  $\text{PbI}_2 \cdot 3\text{PbO} \cdot 2\text{H}_2\text{O}$ ,<sup>13</sup>  $2\text{PbI}_2 \cdot 9\text{PbO} \cdot 2\text{H}_2\text{O}$ ,<sup>13</sup>  $\text{PbI}_2 \cdot 5\text{PbO} \cdot 7\text{H}_2\text{O}$ ,<sup>14</sup>  $\text{PbI}_2 \cdot 6\text{PbO} \cdot 2\text{H}_2\text{O}$ .<sup>12</sup>

The basic chloriodide  $\text{PbI}_2 \cdot \text{PbCl}_2 \cdot \text{PbO}$ , which has been prepared artificially,<sup>15</sup> occurs as the mineral *schweitzerbergite*.

**Lead Tetra-iodide** does not exist, but the quinoline double salt  $(\text{C}_9\text{H}_7\text{NH})_2\text{PbI}_6$  has been prepared<sup>16</sup> by treating the corresponding chloride with potassium iodide, though doubt has been raised whether this compound is really a derivative of quadrivalent lead or a polyiodide of the bivalent metal.<sup>17</sup> The pyridine salt  $(\text{C}_5\text{H}_5\text{NH})_2\text{PbI}_6$  also exists.

**Lead Iodate**,  $\text{Pb}(\text{IO}_3)_2$ , is precipitated as a white powder when alkali iodate is added to lead nitrate solution.<sup>18</sup> When heated it evolves iodine and oxygen, and leaves a mixture of lead iodide and oxide. Lead iodate is one of the numerous very slightly soluble salts whose solubilities in water have been deduced by Kohlrausch<sup>19</sup> from the

<sup>1</sup> Berthelot, *Ann Chim Phys*, 1881, [v], 23, 85.

<sup>2</sup> Mosnier, *Ann Chim Phys*, 1897, [vi], 12, 374.

<sup>3</sup> Bogorodski, *J Russ Phys Chem Ges*, 1891, 26, 216.

<sup>4</sup> Herty, *Amer Chem J*, 1892, 14, 107, 1896, 18, 290, Wells, *Zeitsch anorg Chem*, 1893, 3, 195.

<sup>5</sup> Schiørmackers, *Zeitsch physikal Chem*, 1892, 9, 57, 10, 477.

<sup>6</sup> Wells, *Zeitsch anorg Chem*, 1893, 4, 128.

<sup>7</sup> Wells and Wheeler, *Zeitsch anorg Chem*, 1893, 3, 204.

<sup>8</sup> Hesse, *J. Physical Chem*, 1912, 16, 373.

<sup>9</sup> Thomas, *Compt rend*, 1898, 126, 1349.

<sup>10</sup> Fozzes-Ducon, *Bull Soc chim*, 1897, [iii], 17, 316.

<sup>11</sup> Herty and Boggs, *J. Amer. Chem Soc*, 1897, 19, 820; Thomas, *Bull Soc chim*, 1898, [iii], 19, 598; *Compt. rend.*, 1899, 128, 1231 and 1329; Monkemeyer, *Zeitsch. Kryst. Min.*, 1908, 45, 609.

<sup>12</sup> Stenholm, *Zeitsch anorg Chem*, 1904, 38, 429.

<sup>13</sup> Kuhn, *Arch. Pharm.*, 1817, [ii], 50, 281.

<sup>14</sup> Ditte, *Compt rend*, 1882, 94, 1189.

<sup>15</sup> Bertrand, *Bull. Soc. min. de France*, 1881, 4; Dietzel, *Dingl poly. J.*, 1868, 190, 42.

<sup>16</sup> Classen and Zahorski, *Zeitsch. anorg. Chem.*, 1893, 4, 100.

<sup>17</sup> Elbs and Nubling, *Zeitsch. Elektrochem.*, 1903, 9, 776.

<sup>18</sup> Rammelsberg, *Pogg. Annalen*, 1838, 44, 545.

<sup>19</sup> Kohlrausch, *Zeitsch. physikal Chem*, 1904, 50, 355.

conductivities of their saturated solutions. It is accordingly found that 1 litre of a solution saturated at 18° C. contains 0.019 gram of  $\text{Pb}(\text{IO}_3)_2$ . The basic salt  $\text{Pb}(\text{IO}_3)_2 \cdot 3\text{PbO} \cdot 2\text{H}_2\text{O}$  has been prepared from lead hydroxide and sodium iodate solution, or by the action of sodium hydroxide on lead iodate. It is a white, crystalline powder.<sup>1</sup>

**Lead Periodates.** In common with many other metals lead forms several periodates, most of which may be regarded as basic salts, or salts of polybasic periodic acids.

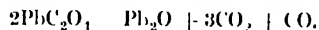
By precipitating lead nitrate solution with sodium iodate, Rammeisberg<sup>2</sup> obtained a white, microcrystalline salt to which he attributed the formula  $\text{Pb}(\text{IO}_3)_2 \cdot 2\text{PbO} \cdot 2\text{H}_2\text{O}$  or  $\text{Pb}_3\text{I}_2\text{O}_{10} \cdot 2\text{H}_2\text{O}$ . When strongly heated this salt loses water, iodine, and oxygen, leaving  $\text{PbI}_2 \cdot 5\text{PbO}$ . According to Kimmings,<sup>3</sup> however, it gradually loses its water at 275° C., leaving the dark yellow anhydrous salt  $\text{Pb}(\text{IO}_3)_2 \cdot 2\text{PbO}$ , and it is converted into the red normal salt  $\text{Pb}(\text{IO}_3)_2$  by prolonged heating with concentrated nitric acid.

Giolitti<sup>4</sup> has obtained rather different results. According to this observer, the salt obtained by adding a dilute acetic acid solution of lead acetate to a cold solution of the salt  $\text{K}_2\text{HIO}_6$ , to which the formula  $\text{Pb}_3\text{I}_2\text{O}_{10} \cdot 2\text{H}_2\text{O}$  was attributed by Rammeisberg, is  $\text{PbHIO}_5$ , and this when heated to 130–140° C. yields the anhydrous salt  $\text{Pb}_2\text{I}_2\text{O}_9$  as a red powder. The hydrated salt  $\text{PbHIO}_5 \cdot \text{H}_2\text{O}$  is formed when a solution of periodic acid is added to a dilute acetic acid solution of lead acetate; and  $\text{PbHIO}_5$  results from the prolonged heating of  $\text{PbHIO}_5$  with water. Lastly, the salt  $\text{Pb}_3\text{I}_2\text{O}_{10} \cdot \text{H}_2\text{O}$ , containing one molecule of water less than Rammeisberg's salt, is probably formed when  $\text{PbHIO}_5$  is heated in dilute nitric acid with lead hydroxide.

## LEAD AND OXYGEN

Lead forms a suboxide,  $\text{Pb}_2\text{O}$ , which does not give rise to any salts, and two fundamental oxides,  $\text{PbO}$  and  $\text{PbO}_2$ . The former of these is basic and also feebly acidic, the latter is feebly acidic and feebly basic but is able also to react as a basic peroxide. These two oxides also combine together to form complex or secondary oxides which are salts,  $2\text{PbO} \cdot 3\text{PbO}_2$  or  $\text{Pb}_5\text{O}_7$ ,  $\text{PbO} \cdot \text{PbO}_2$  or  $\text{Pb}_2\text{O}_3$ ,  $3\text{PbO} \cdot 2\text{PbO}_2$  or  $\text{Pb}_5\text{O}_7$ , and  $2\text{PbO} \cdot \text{PbO}_2$  or  $\text{Pb}_3\text{O}_4$ . The monoxide  $\text{PbO}$  is known in different forms as litharge and massicot; the oxide  $\text{Pb}_2\text{O}_3$  is minium or red lead.

**Lead Suboxide,  $\text{Pb}_2\text{O}$**  Berzelius first observed that when lead is heated below its melting-point in the air its surface becomes covered with a grey film, which appears to be the suboxide. It was later discovered by Dulong that when lead oxalate is heated to 300° C. out of contact with air it yields the suboxide by the reaction



Later observers<sup>5</sup> thought this product was merely a mixture of lead monoxide and metallic lead; but Tanatar<sup>6</sup> has proved that the sub-

<sup>1</sup> Stromholm, *Zeitsch. anorg. Chem.*, 1904, 38, 129.

<sup>2</sup> Rammeisberg, *Pogg. Annalen*, 1838, 44, 515, 1841, 52, 96.

<sup>3</sup> Kimmings, *Trans. Chem. Soc.*, 1889, 55, 148.

<sup>4</sup> Giolitti, *Gazzetta*, 1902, 32, n, 340.

<sup>5</sup> Winklerblech, *J. prakt. Chem.*, 1837, 227; Maunten, *Bull. Soc. chim.*, 1872, 144.

<sup>6</sup> Tanatar, *Zeitsch. anorg. Chem.*, 1901, 27, 301.

oxide is undoubtedly formed by the above reaction, carried out in an atmosphere of carbon dioxide or nitrogen, provided the temperature is kept as low as possible. The product is then a greyish black powder of density 8.342 at 18° C., which is unaltered by dry air or water, but is converted into the monoxide and metallic lead by dilute acids and alkalis. Moreover, the heat of solution of 1 gram-molecule of this substance in acetic acid is 10,048 calories, whilst that of 1 gram-molecule of lead monoxide is 15,500 calories. If, however, the temperature at which lead oxalate is decomposed is too high, a greyish green product results whose molecular heat of solution in acetic acid is 15,500 calories. This product must, therefore, be a mixture of lead monoxide and lead, into which the suboxide is decomposed at high temperature with absorption of 5,452 calories.

The suboxide is also formed by the reduction of the monoxide by hydrogen<sup>1</sup> at a temperature not exceeding 235° C. Further proof that the dark grey powder is not a mixture of lead monoxide and lead is furnished by the fact that mercury dissolves no lead from it, nor sugar solution any lead monoxide. After the powder has been sufficiently heated, however, sugar solution extracts lead monoxide from it, leaving metallic lead behind.

**Lead Monoxide** (*Litharge, Massicot*),  $\text{PbO}$ .—This oxide has been known from antiquity, since it is formed as a scum on the surface of molten lead. If this scum is continuously removed, so that a fresh surface of the molten metal is oxidised, a yellowish grey powder may be collected, which is a mixture of the oxide and the finely divided metal. If this powder is further roasted, it is converted into a yellowish red form of lead oxide known as *massicot*. When the temperature at which the oxidation of the molten metal is so high that the oxide fuses, the solidified product, which is scaly, is called *litharge*. This form of the oxide is obtained in the process of cupellation, by which silver is won from argentiferous lead; hence the name.<sup>2</sup>

The same oxide is produced when lead-vapour burns in the air; formed in this way it has been called *stones plumbi*. Lead monoxide occurs crystallised in rhombic octahedra in a mineral found near Vera Cruz; similar crystals are formed when litharge is allowed to cool slowly; they also occur sometimes as a deposit in lead furnaces.

According to the conditions of its formation lead oxide varies in colour from lemon-yellow to red or yellowish brown. Thus when red lead has been heated in a hard glass tube for the preparation of oxygen, the residue of monoxide is lemon-yellow in colour; and when lead hydroxide is boiled with a 10 per cent. sodium hydroxide solution, a light yellow modification of the oxide is produced, whilst with a very concentrated solution a red modification results.<sup>3</sup>

The different forms of lead monoxide have been investigated by Ruer,<sup>4</sup> who finds that the pure oxide of a brownish yellow colour becomes light yellow when heated to about 620° C. and allowed to cool, again becomes brownish yellow on prolonged rubbing with considerable pressure in a mortar, but returns to the yellow colour when the heating and cooling are repeated. Ruer has further found that

<sup>1</sup> Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 1.

<sup>2</sup> *lithos*, stone, *á lypos*, silver.

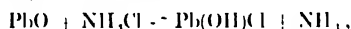
<sup>3</sup> Geuther, *Annalen*, 1883, 219, 56.

<sup>4</sup> Ruer, *Zeitsch. anorg. Chem.*, 1906, 50, 265.

Geuther's red oxide can be changed into the yellow form by prolonged heating at  $700^{\circ}\text{C}.$ ; and he suggests that the yellow form is stable above  $620^{\circ}\text{C}.$ , but unstable below it, and gradually changes into the more stable brownish yellow form, this change being accelerated by friction and pressure. The yellow form of the oxide is considerably more soluble in water than the red form. It is uncertain whether or not the brownish yellow oxide is identical with Geuther's red oxide; the former is more soluble in water than the latter, but this may be due to admixture of the yellow oxide.

The density of the yellow oxide is  $9.50$  to  $9.52^1$  or  $9.28$  to  $9.36^2$ , that of the lighter red oxide being  $9.28^1$  or  $8.71$  to  $9.126^2$ . The melting-point of the oxide lies  $^3$  between  $835^{\circ}\text{C}.$  and  $906^{\circ}\text{C}.$ , its molecular heat of formation is  $50,300$  calories  $^4$  or  $50,800$  calories  $^5$ .

Lead monoxide is easily reduced to metal by various reducing agents, such as hydrogen, carbon monoxide, potassium cyanide, carbon, and carbides. The reduction of the oxide by reaction with the sulphide has already been noticed under the metallurgy of lead. According to Glaser, $^6$   $\text{PbO}$  is reduced by hydrogen to  $\text{Pb}_2\text{O}$  at  $211^{\circ}\text{C}.$  and to metal above  $235^{\circ}\text{C}.$ ; whilst a temperature above  $300^{\circ}\text{C}.$  is necessary for reduction of the oxide to metal by carbon monoxide. $^7$  Chemically, lead monoxide is an amphoteric oxide, that is to say it dissolves in acids as a basic oxide, and in alkalis as an acidic oxide. This oxide reacts with ammonium chloride, producing a basic chloride and ammonia, according to the reaction:



the pressure  $^8$  of the ammonia evolved is a function of the temperature and reaches one atmosphere at about  $12^{\circ}\text{C}.$  When boiled with sodium chloride solution lead oxide produces a basic lead chloride and caustic soda; this reaction is the foundation of Scheele's process of alkali manufacture. This oxide will dissolve in a solution of sucrose, especially in presence of alkali, and may be separated from some other oxides, e.g. arsenious oxide, $^9$  by this means.

Litharge is used in the arts in the manufacture of flint glass, and for glazing earthenware, also for making red lead, white lead, and various salts of lead, and as a drier for painters' oils, such as linseed oil, the setting of which, being due to oxidation, is accelerated by litharge and certain other metallic oxides.

Commercial litharge may contain as impurities iron and copper oxides, as well as carbon dioxide and water absorbed from the air.

**Lead Hydroxides.** Two forms of lead hydroxide are known:  $2\text{PbO} \cdot \text{H}_2\text{O}$  or  $\text{Pb}_2\text{O}(\text{OH})_2$ , and  $3\text{PbO} \cdot \text{H}_2\text{O}$  or  $\text{Pb}_3\text{O}_2(\text{OH})_2$ ; the ortho-hydroxide,  $\text{Pb}(\text{OH})_2$ , appears to be unknown in the solid state.

<sup>1</sup> Ruer, *Zeitsch. anorg. Chem.*, 1906, 50, 265.

<sup>2</sup> Geuther, *Annalen*, 1883, 210, 56.

<sup>3</sup> Ruer, *ibid.* (835 $^{\circ}\text{C}.$ ); Doeltz and Mostowitsch (906 $^{\circ}\text{C}.$ ), *Metallurgie*, 1907, 4, 289; Mostowitsch (883 $^{\circ}\text{C}.$ ), *Metallurgie*, 1907, 4, 647; Schenck and Ris-Loch (879 $^{\circ}\text{C}.$ ), *Ber.*, 1907, 40, 2185, 2947; 1908, 41, 2917.

<sup>4</sup> Thomsen, *J. prakt. Chem.*, 1875, [n], 12, 18, 86.

<sup>5</sup> Berthelot, *Ann. Chem. Phys.*, 1873, [iv], 30, 191.

<sup>6</sup> Glaser, *Zeitsch. anorg. Chem.*, 1907, 36, 13.

<sup>7</sup> Schlagelthausen and Pagel, *Compt. rend.*, 1899, 128, 309.

<sup>8</sup> Isambert, *Compt. rend.*, 1886, 102, 1313; see also O. de Coninck and Arraher, *Bull. Acad. roy. Belg.*, 1907, 713, 800.

<sup>9</sup> Babé and Witter, *Chem. Zentr.*, 1908, 1, 1863.

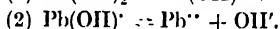
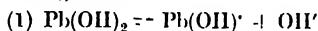
$\text{Pb}_2\text{O}(\text{OH})_2$  is formed by the action of water containing dissolved oxygen on metallic lead; by precipitating lead acetate or other lead salt solution by alkali hydroxide or ammonia<sup>1</sup>; and also by allowing a solution of lead oxide in potassium hydroxide to stand in the air, when the absorbed carbon dioxide displaces hydrated lead oxide from combination with alkali, so that  $\text{Pb}_2\text{O}(\text{OH})_2$  separates in quadratic crystals.<sup>2</sup>

$\text{Pb}_3\text{O}_2(\text{OH})_2$  is prepared<sup>3</sup> from the corresponding basic acetate,  $\text{Pb}_3\text{O}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ , by mixing its saturated aqueous solution with ammonia, and allowing the solution to stand at 25°–30° C., with careful exclusion of air. The hydroxide then separates in shining octahedra. A product of the same composition is obtained by precipitating a lead salt solution with caustic alkali, and drying the precipitate at 100° C.,<sup>4</sup> and also by precipitating a lead salt with baryta water at atmospheric temperature.

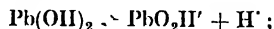
Lead hydroxide is distinctly soluble in water, to which it imparts an alkaline reaction. A saturated solution of  $\text{Pb}_3\text{O}_2(\text{OH})_2$  at 18° C. contains, according to Pleissner,<sup>5</sup> 100.5 m.g.  $\text{PbO}$  per litre. Ruer<sup>6</sup> has found, by the conductivity method, that the solubilities in water at 22° C. of the various forms of lead oxide, with the exception of Genthner's red oxide which is less soluble, lie between  $1.00 \times 10^{-4}$  and  $1.12 \times 10^{-4}$  gram-equivalents per litre; whilst Herz<sup>7</sup> has calculated the solubility of lead hydroxide at 25° C. to be  $0.93 \times 10^{-4}$ . At 130° C. lead hydroxide loses all its water, being converted into the oxide.

It has already been stated that lead monoxide is an amphoteric oxide; thus the hydroxide behaves both as a weak base and a weak acid.

It is possible that in a solution of lead hydroxide in water, which is alkaline in reaction and therefore contains hydroxyl ions, ionisation has proceeded in two stages, thus—



From the work of Berl and Austerweil,<sup>8</sup> however, it appears that only the first reaction is to be considered as taking place, and that ionisation has proceeded to the extent of about 28 per cent. The same authors have determined the solubility of lead oxide in sodium hydroxide solutions of different concentrations and temperatures, and conclude that when the alkali solution is below normal strength the sodium salt  $\text{HPbOONa}$  of the monobasic acid  $\text{HPbOOH}$  is produced in solution, but that with more concentrated alkali solutions the sodium salt  $\text{Pb}(\text{ONa})_2$  of the dibasic acid  $\text{Pb}(\text{OH})_2$  is formed to some extent. Thus, towards weak alkalis lead hydroxide behaves as if it were ionised thus:



<sup>1</sup> Schaffner, *Ann. Chem.*, 1844, 51, 175.

<sup>2</sup> Ludeking, *Amer. Chem. J.*, 1891, 13, 120.

<sup>3</sup> Payen, *Ann. Chim. Phys.*, 1837, [n], 66, 49, 1866, [iv], 8, 302.

<sup>4</sup> Mulder, *J. prakt. Chem.*, 1879, 19, 79.

<sup>5</sup> Pleissner, *Arbeiten Kaiserl. Gesundheitsamte*, 1907, 26, 384; see also *Chem. Zentr.* 1907, [n], 1035.

<sup>6</sup> Ruer, *Zeitsch. anorg. Chem.*, 1906, 50, 273.

<sup>7</sup> Herz, *Zeitsch. anorg. Chem.*, 1910, 68, 421.

<sup>8</sup> Berl and Austerweil, *Zeitsch. Elektrochem.*, 1907, 13, 165.

## LEAD AND ITS COMPOUNDS

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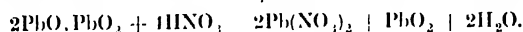
and the dissociation constant of this acid at 18° C. is found to be  $1.1 \times 10^{-12}$ , which shows lead hydroxide to be a weaker acid than phenol.

Hantzsch,<sup>1</sup> however, finds no evidence that hydroxides of the type  $M(OH)_2$  can behave as dibasic acids, and regards their salts as always derived from acids of the formic acid type  $HMOOH$ . Moreover, he has shown that the hydroxides of lead, tin, and germanium are feeble acids whose strengths increase in the order in which the metals are named.

Lead monoxide dissolves in lime and heavy water, forming yellow solutions, and also in strong solutions of calcium and strontium chloride. Lead hydroxide combines with polyhydric alcohols and hydroxy-carboxylic acids to form complex compounds in solution in which the lead is very little ionised.<sup>2</sup> Alkali plumbate solution is used as a mordant in cotton dyeing.

**Lead Dioxide** (*Lead Peroxide, Peach-coloured Oxide of Lead*),  $PbO_2$ . This oxide occurs naturally as *plattnerite*, crystallised in hexagonal prisms, and may be obtained artificially in six-sided tablets. It was discovered by Scheele, who found that red lead is turned brown by chlorine water. Priestley noticed that nitric acid similarly changes red lead, but Proust and Vauquelin<sup>3</sup> were the first to examine this compound systematically.

**Preparation.**—Lead dioxide may be prepared in many ways. It may be obtained from the monoxide, from lead salts, or from red lead by the action upon them of chlorine or bromine water, preferably in presence of alkali, by fusing litharge with potassium chlorate, or by oxidising it with alkaline permanganate or potassium ferricyanide; also by the action of ozone (Schonbein) hydrogen peroxide,<sup>4</sup> and persulphates on lead salts, as well as by the hydrolysis of plumbic salts. An interesting example of this latter reaction is shown by dissolving red lead in glacial acetic acid and then pouring the solution into water. Red lead is a compound of  $PbO$  and  $PbO_2$ , and its solution in glacial acetic acid contains lead di- and tetra-acetates, the latter of which is hydrolysed by water, with precipitation of the dioxide. If red lead is digested with dilute nitric acid it does not dissolve as a whole, because plumbic nitrate is not formed. The result is, therefore, the formation of lead dimitate in solution with separation of the dioxide, thus:



Another important method of obtaining lead peroxide is by electrolytic oxidation, so that it separates at the anode when a suitable lead solution is electrolysed. When electrolysis takes place in alkaline solution the crystalline hydrate  $H_2PbO_4$  is deposited, when in neutral or acid solution the anhydride is obtained, and its separation serves to estimate lead electrolytically.<sup>5</sup> Lead dioxide is also prepared by the electrolysis of a solution of sodium chloride in which the monoxide is suspended.<sup>6</sup> The sodium hydroxide formed by electrolysis dissolves

<sup>1</sup> Hantzsch, *Zeitsch. anorg. Chem.*, 1902, 30, 289.

<sup>2</sup> Kahlenberg, *Zeitsch. physikal. Chem.*, 1895, 17, 777.

<sup>3</sup> Vauquelin, *Ann. Chim. Phys.*, 1807, [i], 62, 221.

<sup>4</sup> Bayley, *Phil. Mag.*, 1879, [vi], 7, 126; Zolner, *Bull. Soc. chim.*, 1913, [iv], 13, 81.

<sup>5</sup> Wolman, *Zeitsch. Elektrochem.*, 1897, 3, 537; Holland, *Compt. rend.*, 1903, 136, 229;

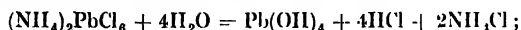
Sand, *Trans. Farad. Soc.*, 1910, 5, 207.

<sup>6</sup> Chemische Fabrik Griesheim-Elektron, German Patent, 124,512.

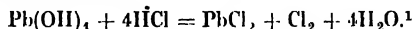


the lead oxide forming plumbite, and this is then oxidised by the hypochlorite present with precipitation of the dioxide.

Colloidal, hydrated, lead dioxide is formed by the hydrolysis of ammonium plumbichloride by much water, thus :



the solution, which is brown, is unstable, and soon becomes colourless on account of the reaction :

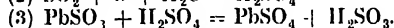
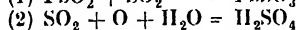


Lead dioxide is prepared commercially by the method of Liebig and Wöhler, which consists in fusing 4 parts of litharge with 1 of potassium chlorate and 8 of nitre ; and also by a modern process in which lead sulphate is mixed with magnesia, and the mixture is suspended in hot water and treated with chlorine <sup>2</sup> :



*Properties.*—Lead dioxide, which is called puce-coloured oxide, is perhaps more accurately described as chocolate-coloured. In its natural form it is a brown or grey crystalline powder which has a density of 9.39 to 9.45. The density of the synthetic substance lies between 8.90 and 9.19. Its molecular heat of formation from lead monoxide is 12,100<sup>3</sup> or 10,100<sup>4</sup> calories, corresponding to a heat of formation from its elements of 62,400 or 60,400 calories.

Lead dioxide is chiefly employed in the chemical laboratory, and in the arts, as an oxidising agent. When it is heated above 310° C. it loses half its oxygen and is converted into the monoxide ; at a lower temperature, however, under the influence of sunlight it yields red lead,  $\text{Pb}_3\text{O}_4$  ; but, according to Reinders and Hamburger,<sup>5</sup> red lead is not formed when lead dioxide is heated. When the dioxide is triturated with red phosphorus or sulphide of phosphorus the mixture inflames ; on this account it is used in making Swedish matches ; when it is rubbed with ordinary phosphorus an explosion takes place. Lead dioxide combines spontaneously with sulphur dioxide gas, becoming red hot and forming lead sulphate ; when, however, it is suspended in sulphurous acid solution the following reactions take place <sup>6</sup> :



The dioxide likewise combines quantitatively with nitrogen peroxide to form lead nitrate, and also oxidises ammonia with production of the same salt. Hydrochloric acid is oxidised when boiled with lead dioxide, with liberation of chlorine, which may be passed into potassium iodide solution : the dioxide may then be estimated by the titration of the liberated iodine. Probably some lead tetrachloride is formed in this reaction and decomposed again by heat.

<sup>1</sup> Gutbier and Sauer, *Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 171.

<sup>2</sup> Friderick, Mallet, and Guye, *Mon. scient.*, 1906, [iv], 20, ii, 514.

<sup>3</sup> Tscheltzow, *Compt. rend.*, 1885, 100, 1458.

<sup>4</sup> Streintz, *Wied. Annalen*, 1894, 53, 698.

<sup>5</sup> Reinders and Hamburger, *Zeitsch. anorg. Chem.*, 1914, 89, 71.

<sup>6</sup> Marino, *Zeitsch. anorg. Chem.*, 1908, 56, 233.

Lead dioxide oxidises chromic hydroxide in presence of alkali to chromate, and from the yellow solution lead chromate may be precipitated by acetic acid. It also oxidises a manganous salt in presence of nitric acid to permanganate, both these reactions are employed in qualitative analysis. Phosphorus trichloride when warmed reacts vigorously with lead dioxide, lead phosphate, phosphoryl chloride and lead chloride being formed, and hypophosphorous acid in aqueous solution produces lead phosphate.

Hydrogen peroxide in neutral solution is decomposed catalytically by lead dioxide, but in acid solution a quantitative reaction takes place thus:

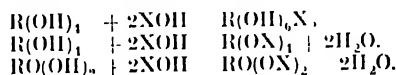


so that lead may be estimated by titration with hydrogen peroxide solution after oxidation to dioxide by bromine in presence of alkali.<sup>1</sup> Oxalic acid in presence of nitric acid is also oxidised to carbon dioxide and water by lead peroxide, and this reaction serves for the volumetric estimation of this latter substance.

Lead dioxide is reduced by hydrogen, the reduction beginning at 189° C. and yielding lead monoxide, which is not further reduced till the temperature is raised to 211° C.<sup>2</sup> Carbon reduces lead dioxide at 260° C.; carbon monoxide combines with it at 80° C., forming lead carbonate. Lead peroxide, either moist or dry, glows when hydrogen sulphide gas is passed over it, and the gas burns with a characteristic lead flame.<sup>3</sup>

Lead dioxide is soluble in water to the minutest extent; it is distinctly more soluble in mineral acids, presumably with the formation of plumbic salts. Under no conditions does it give rise to hydrogen peroxide, and this may be taken to show that it is not a superoxide like barium dioxide, but a polyoxide, that is a compound of quadrivalent lead, having the constitution  $\text{O} \cdot \text{Pb} \cdot \text{O}$ .

Like lead monoxide, the dioxide is an amphoteric oxide, but in accordance with the larger proportion of oxygen it contains its basic properties are very feeble, whilst its acidic properties are more pronounced than are those of the monoxide. The plumbates will be considered here, the plumbic oxy-salts subsequently. According to Bellucci and Parravano,<sup>4</sup> there are three types of plumbates, as well as of plumbates and stannates:  $\text{R}(\text{OH})_6\text{X}_2$ ,  $\text{R}(\text{OX})_4$ , and  $\text{RO}(\text{OX})_2$ , derived from the ortho- or meta-acids, thus:



**Plumbic Acids.**—Of the three types of plumbic acid indicated above,  $\text{H}_2[\text{Pb}(\text{OH})_6]$  may possibly exist,  $\text{Pb}(\text{OH})_4$  is unknown, but  $\text{H}_2\text{PbO}_3$  has been prepared.

**Hexahydroxyplumbic Acid,  $\text{H}_2[\text{Pb}(\text{OH})_6]$ , and its Salts.**—When dilute acetic acid is added to a solution of potassium plumbate cooled with ice, a flocculent precipitate separates which is lighter in colour

<sup>1</sup> Schlossberg, *Zeitsch. anal. Chem.*, 1902, 41, 735.

<sup>2</sup> Glaser, *Zeitsch. anorg. Chem.*, 1903, 36, 1.

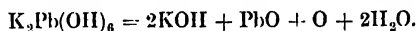
<sup>3</sup> Vanino and Hauser, *Ber.*, 1900, 33, 625.

<sup>4</sup> Bellucci and Parravano, *Gazzetta*, 1905, 35, ii, 500.

even than ferric hydroxide. It gradually turns brown, however, and when dried in the air produces lead dioxide. This precipitate may be  $H_2[Pb(OH)_6]$ , because potassium plumbate, from which it is derived, is believed to be  $K_2[Pb(OH)_6]$ .

**Colloidal Plumbic Acid** is obtained by the dialysis of potassium plumbate solution, which is completely hydrolysed at ordinary atmospheric temperature into  $PbO_2 \cdot Ag + 2KOH$ .<sup>1</sup> The hydrosol finally obtained, which contains  $PbO_2$  and  $K_2O$  in the ratio 98.13 : 1.87, may be filtered, boiled, evaporated to a syrup, and again dissolved in water. The small amount of potash present—the “Solbildner”—is of the same order as the amounts of hydrochloric acid necessary for the existence of the hydrosols of aluminium, chromic and ferric hydroxides.

**Potassium Plumbate**,  $K_2PbO_3 \cdot 3H_2O$  or  $K_2Pb(OH)_6$ , was prepared by Frémy<sup>2</sup> and Seidel,<sup>3</sup> and subsequently by Bellucci and Parravano,<sup>4</sup> who heated 100 grams of potassium hydroxide in a silver dish, with 20–30 grams of water, and added as much lead dioxide, made into a paste with water, as would dissolve. The filtered solution was then evaporated *in vacuo* over sulphuric acid, when colourless, rhombohedral crystals were obtained, which were isomorphous with potassium stannate and platinate. This salt is believed to have its water intimately combined, and not simply as water of crystallisation, both on account of its isomorphism with the similarly constituted stannate and platinate, and because the water cannot be driven off at 100° C., but is only set free when the salt is strongly heated so as to undergo the following change :



To sodium plumbate Hohnel<sup>5</sup> attributed the formula  $Na_2PbO_3 \cdot 6H_2O$ ; but, according to Bellucci and Parravano, there is no sufficient reason for supposing that its constitution differs from that of the potassium salt.

By measurements of electric conductivity, and degree of hydrolysis of ethyl acetate, Parravano and Calcagni<sup>6</sup> have determined the extent to which potassium plumbate is hydrolysed in aqueous solution; and they find that whilst a concentrated solution contains a small proportion of undecomposed salt, the amount of this diminishes on dilution; and that in a  $\frac{1}{161.9}$  molecular solution all the plumbate has been resolved into alkali and colloidal plumbic acid. The series lead, silicon, tin, represents the order of increasing acidity of these elements.

**Lead Plumbate.**—A hydrate of lead sesquioxide, which probably has the constitution  $Pb[Pb(OH)_6]$ , is obtained as an amorphous, orange-yellow precipitate by decomposing an alkaline solution of the monoxide with potassium plumbate (Bellucci and Parravano).

**Salts of Orthoplumbic Acid.**  $Pb(OH)_4$ .—Although orthoplumbic acid is unknown, its alkaline-earth salts have been prepared, and its lead salt is the important compound known as red lead.

<sup>1</sup> Bellucci and Parravano, *Atti R. Accad. Lincei*, 1906, [v], 15, ii, 542, 631.

<sup>2</sup> Frémy, *Ann. Chim. Phys.*, 1844, [iii], 12, 488.

<sup>3</sup> Seidel, *J. prakt. Chem.*, 1879, 20, 200.

<sup>4</sup> Bellucci and Parravano, *Zeitsch. anorg. Chem.*, 1906, 50, 101, 107.

<sup>5</sup> Hohnel, *Arch. Pharm.*, 1894, 232, 222.

<sup>6</sup> Parravano and Calcagni, *Gazzetta*, 1907, 37, ii, 28.

## LEAD AND ITS COMPOUNDS

**Calcium Orthoplumbate**,  $\text{Ca}_2\text{PbO}_4$ , is formed by heating lime with lead dioxide, or with the monoxide in presence of air.<sup>1</sup> This latter reaction is interesting, since it is the presence of a base which secures the oxidation of monoxide completely to dioxide.<sup>2</sup> The absorbed oxygen is evolved again when the salt is more strongly heated; the reaction is thus a reversible one, and it has been proposed to employ it for abstracting oxygen from the air, and also to use the salt as an oxidising agent. The dissociation pressure of calcium plumbate has been studied by Le Châtelier.<sup>3</sup>

With water the crystalline hydrate  $\text{Ca}_2\text{PbO}_4 \cdot 11\text{H}_2\text{O}$  is formed. The salt is stable in an fire from carbon dioxide, but when it is suspended in water and treated with dilute acids or carbon dioxide lead dioxide separates.

Strontium and barium plumbates are similar to the calcium salt.

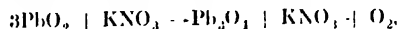
**Lead Orthoplumbate, Red Lead** (*Minium, Paris Red, Saturn Cinnabar*),  $\text{Pb}_3\text{O}_4$ —Pliny appears to have been acquainted with this oxide, which he describes as *minium*, though probably cinnabar and red sulphide of arsenic were confused with it. Dioscorides states that it can be obtained from white lead, and Geber describes its preparation.

Red lead is usually prepared by heating the yellow, powdery form of lead monoxide, known as massicot, to dull redness (100° C.) for twenty-four hours in a reverberatory furnace with a plentiful air-supply, or in barrel-shaped vessels open at the ends to allow of air circulation. The mass is frequently stirred, and samples are removed from time to time, and allowed to cool, to see if the proper scarlet tint has been attained. White lead, however, is frequently the starting-point for the manufacture of red lead. Red lead is also formed when lead monoxide and dioxide are heated together in the right proportion, as well as by heating lead monoxide with nitre.<sup>4</sup> Finely divided lead also is oxidised spontaneously in the air to red lead.<sup>5</sup> On account of its usual manner of preparation red lead is liable to contain the monoxide which has escaped oxidation; this may be removed by repeatedly digesting the powder with lead acetate solution.

Pure red lead may be prepared by heating lead monoxide with potassium nitrate, according to the reaction



and extracting unchanged monoxide with lead acetate solution; or by heating the dioxide and potassium nitrate to 170° C.,



and extracting the resulting mass with potassium hydroxide or lead acetate solution.<sup>6</sup>

Red lead crystallises from fused nitre in small prisms; and it has a density of 8.62 to 9.08. When this oxide is heated it turns violet and then black, but regains its scarlet colour on cooling. This is an

<sup>1</sup> Kassner, *Arch. Pharm.*, 1890, 228, 109; 1891, 232, 375; 1893, 253, 501.

<sup>2</sup> Compare the atmospheric oxidation of  $\text{Cr}_2\text{O}_3$  and  $\text{MnO}_2$  in presence of alkali, to chromate and manganate.

<sup>3</sup> Le Châtelier, *Compt. rend.*, 1894, 117, 109.

<sup>4</sup> Burton, *Dingler's poly. J.*, 1863, 167, 361.

<sup>5</sup> Schönbein, *J. prakt. Chem.*, 1858, 74, 323.

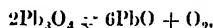
<sup>6</sup> Milbauer, *Chem. Zeit.*, 1914, 38, 477, 559, 566, 587.

enantiotropic change, which has been studied by Le Chatelier,<sup>1</sup> who estimates the transition temperature of the two forms to be 580° C., whilst the melting-point of the compound is 830° C., and its dissociation pressures are :

Temperature, ° C. . . . .	445°	500°	555°	636°
Dissociation Pressure, mm. Hg. . . . .	5	60	183	768

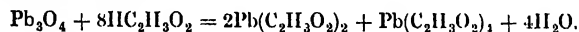
The conditions of formation of red lead from lead monoxide by the absorption of oxygen have been studied by Milbauer,<sup>2</sup> who finds that this absorption which begins at ordinary temperature becomes sufficient to be measured at 240° C. ; that at 320°–450° C., whilst the amount of absorption has increased the product has not become red, but is brown, and probably contains the sesquioxide  $\text{Pb}_2\text{O}_3$  ; above 450° C., however, a red colour appears and red lead is formed, whilst at 470°–480° C. 100 per cent. of red lead is formed under pressure.<sup>3</sup> Red lead is completely decomposed at 530° C. in a vacuum, but the temperature of complete decomposition is higher when air or oxygen is present. The curve of decomposition has breaks showing the formation of the oxides  $\text{Pb}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}$ .<sup>4</sup>

Reinders and Hamburger,<sup>5</sup> however, who have studied the thermal dissociation of red lead, according to the reaction



state that the pressure-temperature curve between 445° C. and 607° C. is regular.

Dry chlorine converts red lead into lead dichloride and oxygen. Red lead is practically insoluble in water ; dilute acids decompose this oxide forming a salt of bivalent lead, with separation of lead dioxide ; but with concentrated acids the unstable plumbic salts are formed. For example, glacial acetic acid produces a mixture of the two acetates, thus :



According to its formula red lead should contain 34.9 per cent. of lead dioxide ; the commercial product, however, generally contains about 26 per cent. of the latter oxide ; and besides lead monoxide it may contain as impurities oxide of iron, powdered heavy spar, and brick-dust, which should be regarded as adulterants. Various methods are available for the analysis of red lead ; these depend upon its oxidising power, which is a measure of the proportion of lead dioxide contained in the specimen. The sample may be heated with hydrochloric acid, and the evolved chlorine passed into potassium iodide, the liberated iodine being titrated with thiosulphate (Bunsen) ; or the iodine may be liberated directly from potassium iodide without distillation,<sup>6</sup> and similarly titrated. Another method depends upon the oxidation of oxalic acid

<sup>1</sup> Le Chatelier, *Bull. Soc. chim.*, 1897, [iii], 17, 791.

<sup>2</sup> Milbauer, *Chem. Zeit.*, 1909, 33, 513, 522, 950, 960.

<sup>3</sup> Milbauer, *Chem. Zeit.*, 1912, 36, 1436, 1484.

<sup>4</sup> Milbauer, *Chem. Zeit.*, 1910, 34, 138, 1341 ; Brown and Nees, *J. Ind. Eng. Chem.*, 1912, 4, 867.

<sup>5</sup> Reinders and Hamburger, *Zetsch. anorg. Chem.*, 1914, 89, 71.

<sup>6</sup> Topp, *Zetsch. anal. Chem.*, 1887, 26, 296.

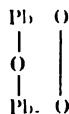
to carbon dioxide and water by the red lead<sup>1</sup>; excess of oxalic acid is used, and what remains is titrated with permanganate.

On account of its fine colour, red lead is used as a pigment; it is also employed as a cement for steam joints, in the manufacture of secondary batteries, and for making flint glass.

**Metaplumbic Acid and its Salts.**—Metaplumbic acid,  $\text{PbO}_2 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{PbO}_3$ , is formed at the anode during the electrolysis of a feebly alkaline solution of lead sodium tartrate.<sup>2</sup> It is a black, lustrous solid, having a density of 6.267.

**Calcium Metaplumbate**,  $\text{CaPbO}_3$ , is formed when the orthoplumbate is digested with water and sodium peroxide.<sup>3</sup> It is a white, crystalline powder, which, according to analysis, contains four molecules of water. The same salt is formed, mixed with calcium hydroxide, when  $\text{Ca}_2\text{PbO}_4 \cdot \text{H}_2\text{O}$  is heated to 240–250° C. so as to lose three-quarters of its water.<sup>4</sup> The orthoplumbate is regenerated when the meta-salt is heated with lime to 500° C. *Silver, zinc* and *cupric metaplumbates* have been prepared from the calcium salt.<sup>5</sup>

**Lead Metaplumbate**,  $\text{Pb}_2\text{PbO}_3$ , prepared from the calcium salt,<sup>7</sup> is identical with *lead sesquioxide*,  $\text{Pb}_2\text{O}_3$ ,<sup>8</sup> to which Marino<sup>6</sup> attributes the constitutional formula.



This oxide is, however, usually prepared by carefully adding hypochlorite solution to a cold solution of alkali plumbite.<sup>7</sup> It may also be obtained by adding very dilute ammonia to an acetic acid solution of red lead, or by heating lead monoxide or dioxide to 350° C. in air or oxygen, oxygen being absorbed or evolved so that  $\text{Pb}_2\text{O}_3$ , the most stable product at this temperature, may be formed. Lead sesquioxide is a reddish yellow amorphous powder which behaves towards acids similarly to red lead, in accordance with the fact that it is lead metaplumbate. A hydrated form of lead sesquioxide, to which Billner and Parravano<sup>8</sup> attribute the constitutional formula  $\text{Pb}[\text{Pb}(\text{OH})_6]$ , is obtained by precipitating an alkaline solution of lead monoxide with potassium plumbate.

**Basic Lead Plumbate.**—A product intermediate between  $\text{Pb}_3\text{O}_4$  and  $\text{Pb}_2\text{O}_3$  exists, having the empirical composition  $\text{Pb}_5\text{O}_7 \cdot 3\text{H}_2\text{O}$ , which may be written  $3\text{PbO} \cdot 2\text{PbO}_2 \cdot 3\text{H}_2\text{O}$ . It is obtained<sup>9</sup> as an orange-coloured powder by precipitating with alkali hydroxide a solution of lead nitrate to which hydrogen peroxide has been added. It is not simply a mixture of lead monoxide and dioxide, since cold caustic alkali extracts none of the former oxide from it.

<sup>1</sup> Lux, *Zeitsch. anal. Chem.*, 1889, 19, 153, see also Bock, *Zeitsch. anal. Chem.*, 1908, 74, 465, and Marchesi, *Gazz. Ital.*, 1907, 37, ii, 259.

<sup>2</sup> Wernicke, *Pogg. Annalen*, 1870, 139, 132, 141, 109.

<sup>3</sup> Grützner and Hohnel, *Arch. Pharm.*, 1895, 233, 312, 1899, 234, 395.

<sup>4</sup> Kassner, *Arch. Pharm.*, 1895, 233, 501.

<sup>5</sup> Jacquelin, *J. prakt. Chem.*, 1851, 53, 151.

<sup>6</sup> Marino, *Zeitsch. anorg. Chem.*, 1909, 62, 173.

<sup>7</sup> Schaffner, *Annalen*, 1844, 51, 175.

<sup>8</sup> Bellucci and Parravano, *Zeitsch. anorg. Chem.*, 1906, 50, 101, 107.

<sup>9</sup> Braunor, *Zeitsch. anorg. Chem.*, 1894, 7, 2.

Another oxide, having the empirical composition  $\text{Pb}_3\text{O}_5$ , and containing 4.2 per cent. of active oxygen, is formed when the monoxide is heated with oxygen in a pressure furnace as long as combination takes place.<sup>1</sup> This oxide, which is dark brown, and resembles lead dioxide in appearance, may be regarded as lead pyroplumbate,  $2\text{PbO} \cdot 3\text{PbO}_2$ , or  $\text{Pb}_2(\text{Pb}_3\text{O}_8)$ .

It should be added, however, that Reinders and Hamburger,<sup>2</sup> who have studied the thermal dissociation of red lead and lead dioxide, do not confirm the existence of the intermediate oxides  $\text{Pb}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_7$ ,  $\text{Pb}_5\text{O}_9$ .

### LEAD AND SULPHUR

**Lead Sulphide**,  $\text{PbS}$ , occurs in nature, and is the principal ore of lead. This ore has been known since the time of the ancients as *galena*, but that it contained sulphur was not recognized till modern times, although Boyle was aware that lead could be obtained from it by heating it with scrap-iron. Another name for the ore is *lead glance*. It occurs in dark grey masses, having a metallic lustre, crystallised in regular cubes or octahedra, and shows a well-defined cubic cleavage. Galena has a hardness of 2.5 and a density of 7.51 to 7.76.

Artificial lead sulphide may be prepared in the dry way, or by precipitating a lead salt solution with hydrogen sulphide or other soluble sulphide.

When lead is heated in sulphur vapour the metal burns and forms crystals or fused globules of the sulphide. The sulphide is also formed when lead oxide is heated with excess of sulphur. The formation of lead sulphide by the action of atmospheric hydrogen sulphide on lead pigments is well known; it accounts for the darkening of oil-paintings by age, and of structures coated with paint into the composition of which white lead enters. On this account no part of a chemical laboratory should be covered with lead paint. Further, it is frequently observed that powders containing lead compounds darken after exposure for a short time to the air of a laboratory in which hydrogen sulphide is being employed.

When lead sulphide is precipitated by hydrogen sulphide from a solution of lead acetate or nitrate the precipitate is amorphous, but when it is formed in a dilute solution containing free nitric acid, it is obtained crystallised in microscopic cubes.

Whilst crystallised lead sulphide is dark grey the precipitated sulphide is brownish black. The two forms differ in density; the density of the crystallised compound is 7.48<sup>3</sup> and of the amorphous 7.13.<sup>4</sup> The melting-point of lead sulphide lies in the region of 1000° C.; that of galena has been estimated to be 1120° C.<sup>5</sup>; the sulphide, however, sublimes below its melting-point, and a sublimate has been observed in a vacuum as low as 600° C.,<sup>6</sup> consisting of cubes which may be 1.5 mm. in diameter. On account of this property crystals of sublimed galena are often obtained in lead works. The molecular

<sup>1</sup> Fischer and Moetze, *Zeitsch. anorg. Chem.*, 1912, 75, 16.

<sup>2</sup> Reinders and Hamburger, *Zeitsch. anorg. Chem.*, 1914, 89, 71.

<sup>3</sup> Mourlot, *Compt. rend.*, 1896, 123, 54.

<sup>4</sup> Clarke, *Constants of Nature*, Washington, 1888.

<sup>5</sup> Biltz, *Zeitsch. anorg. Chem.*, 1908, 59, 273.

<sup>6</sup> Damm and Kraft, *Ber.*, 1907, 40, 4775.

## LEAD AND ITS COMPOUNDS

Heat of formation of precipitated lead sulphide is 20,400<sup>1</sup> or 20,800<sup>2</sup> calories; its specific heat, which varies somewhat with temperature, has a mean value of about 0.068.<sup>3</sup>

Lead sulphide is reduced to metal when heated in a current of hydrogen; chlorine converts it into chloride with the simultaneous formation of sulphur dichloride,  $\text{SCl}_2$ , but in presence of water-vapour forms the peroxide. Dilute nitric acid dissolves lead sulphide with the formation of nitrate in solution and separation of sulphur. At the same time some of this sulphur is oxidised to sulphuric acid with the consequent formation of lead sulphate, and this is specially the case when the concentrated acid is employed, so that the sulphide appears to be directly oxidised to sulphate. Hot concentrated hydrochloric acid dissolves lead sulphide with evolution of hydrogen sulphide; and this sulphide is by no means insoluble in the dilute acid, so that traces of lead may remain in solution after the passage of hydrogen sulphide if too much hydrochloric acid was present and in the course of qualitative analysis will subsequently be precipitated as hydroxide by ammonia. Several other sulphides are less soluble in water than lead sulphide, e.g. cupric and silver sulphides. Consequently double decomposition occurs when freshly precipitated lead sulphide is shaken with solutions of cupric or silver salts. The solubility in water of precipitated lead sulphide at 18° C. is  $3.60 \times 10^{-6}$  gram-molecules per litre, that of the crystallised sulphide is about a third this value.<sup>4</sup> When lead sulphide is fused with caustic soda in the air, the sulphide is oxidised to sulphate, which dissolves in the soda.<sup>5</sup> This is an example of the influence of a solvent upon oxidation, since the reaction depends upon the solubility of lead sulphate in caustic soda, it is analogous to the oxidation of manganese and chromic compounds to manganate and chromate under the same conditions. Similarly, precipitated lead sulphide is oxidised and dissolved when it is boiled with sodium peroxide and water.

**Lead Sulphohalides.**—The following sulphohalides of lead are known:  $\text{PbS} \cdot \text{PbCl}_2$ ,  $\text{PbS} \cdot 4\text{PbCl}_2$ ,  $\text{PbS} \cdot \text{PbBr}_2$ ,  $\text{PbS} \cdot 4\text{PbBr}_2$ ,  $\text{PbS} \cdot \text{PbI}_2$ ,  $\text{PbS} \cdot 4\text{PbI}_2$ . No sulphofluoride is known.

**Lead Sulphochlorides.**—It is well known that when hydrogen sulphide gas is passed into a solution of a lead salt containing much hydrochloric acid a dark red precipitate is obtained, which turns black if the solution is diluted and hydrogen sulphide is again passed into it. This red compound is a lead sulphochloride which was originally supposed to be  $3\text{PbS} \cdot 2\text{PbCl}_2$ ,<sup>6</sup> but is very probably  $\text{PbS} \cdot \text{PbCl}_2$ .<sup>7</sup> Another sulphochloride, having the composition  $\text{PbS} \cdot 4\text{PbCl}_2$ , is obtained by diluting a solution of lead sulphide in concentrated hydrochloric acid.<sup>8</sup>

**Lead Sulphobromides.**— $\text{PbS} \cdot \text{PbBr}_2$  and  $\text{PbS} \cdot 4\text{PbBr}_2$  can be prepared quite similarly to the corresponding sulphochlorides.<sup>8</sup>

**Lead Sulphoiodide.**  $\text{PbS} \cdot 4\text{PbI}_2$  may be obtained either by diluting a solution of lead sulphide in concentrated hydroiodic acid, or by adding

<sup>1</sup> Thomaen, *Thermochimische Untersuchungen*, 1883, iii, 453.

<sup>2</sup> Berthelot, *Ann. Chem. Phys.*, 1875, [v], 4, 187.

<sup>3</sup> Streimtz, *Boltzmann-Festschrift*, 1904.

<sup>4</sup> Weigel, *Zeitsch. physikal. Chem.*, 1907, 55, 293.

<sup>5</sup> Mourlot, *Compt. rend.*, 1890, 123, 54.

<sup>6</sup> Hunenfeld, *J. pract. Chem.*, 1836, 7, 27.

<sup>7</sup> Parmentier, *Compt. rend.*, 1892, 114, 299.

<sup>8</sup> Lenher, *J. Amer. Chem. Soc.*, 1896, 17, 511; 1901, 23, 680.



an aqueous solution of hydrogen sulphide to a solution of lead iodide in the same acid, or in concentrated potassium iodide solution.<sup>1</sup>

**Lead chlorothiobismuthite**,  $\text{PbS} \cdot \text{Bi}_2\text{S}_3 \cdot 2\text{BiSCl}$ , and the corresponding bromo- and iodo-compounds have been prepared by Ducatte.<sup>2</sup>

**Lead Polysulphide**.—A purple-red polysulphide of lead, having the composition  $\text{PbS}_5$ , is formed when a solution of calcium polysulphide is added in excess to a dilute solution of lead nitrate cooled to  $0^\circ \text{C}$ .; above  $10^\circ \text{C}$ . this compound decomposes into lead monosulphide and free sulphur.<sup>3</sup>

It was observed by Hofmann and Wollf<sup>4</sup> that when lead halides dissolved in dilute sodium thiosulphate solution are exposed to light precipitates are formed which are not lead sulphide, this alone being formed from the solutions in diffused light or in the dark. In the case of the chloride a red precipitate of  $\text{Pb}_3\text{S}_4\text{Cl}_2$  is formed, whereas from the iodide  $\text{Pb}_3\text{S}_4\text{I}_2$  separates as a copper-red powder. The latter compound is also formed by the action of yellow ammonium sulphide solution on lead iodide.

**Lead Sulphite**,  $\text{PbSO}_3$ , is obtained as a white precipitate when alkali sulphite is added to lead nitrate solution, or sulphurous acid to lead acetate solution.<sup>5</sup> This salt is easily oxidised and decomposed by acids; heating converts it into a mixture of sulphide and sulphate.

**Lead Sulphates**—Lead forms the two sulphates  $\text{PbSO}_4$  and  $\text{Pb}(\text{SO}_4)_2$ , in which the metal is bi- and quadri-valent respectively. They are conveniently known as lead sulphate and plumbic sulphate.

**Lead Sulphate**,  $\text{PbSO}_4$ , is found naturally as the mineral *anglesite* or lead vitriol, which often occurs in large transparent crystals, isomorphous with those of celestine and heavy spar. The salt may be prepared artificially by precipitating a lead salt solution with sulphuric acid or a soluble sulphate. Thus obtained it is a white, microcrystalline powder. It may be obtained in a more distinctly crystalline form by causing it to be produced slowly; thus if the end of a platinum wire, covered with fused lead chloride, is allowed to dip into a layer of water which has been poured upon the surface of a saturated solution of potassium sulphate, crystals of lead sulphate are gradually formed.<sup>6</sup> Lead sulphate is also formed by the interaction of lead dioxide and sulphur dioxide.

For commercial purposes lead sulphate is prepared as follows: Granulated lead is dissolved in acetic acid in steam-heated vats. The liquor is then poured off into a large wooden tank, and lead sulphate precipitated by the addition of sulphuric acid. After standing, the clear liquid, consisting of acetic acid, is pumped back into the vats to act upon a further supply of lead, whilst the precipitated lead sulphate is washed and dried.

Natural lead sulphate has a density of 6.30 to 6.39; the density of the synthetic salt is 6.17. The melting-point of the pure salt appears to be above  $1100^\circ \text{C}$ ., but is difficult to determine on account of the loss of sulphur trioxide at this high temperature.<sup>7</sup> There is, however,

<sup>1</sup> Lenher, *J. Amer. Chem. Soc.*, 1895, 17, 511; 1901, 23, 680.

<sup>2</sup> Ducatte, *Compt. rend.*, 1902, 134, 1061.

<sup>3</sup> Bodroux, *Compt. rend.*, 1900, 130, 1397.

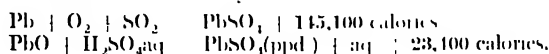
<sup>4</sup> Hofmann and Wollf, *Ber.*, 1904, 37, 249.

<sup>5</sup> Seubert and Elton, *Zeitsch. anorg. Chem.*, 1893, 4, 44.

<sup>6</sup> Manross, *Annalen*, 1852, 82, 360.

<sup>7</sup> Ramsay and Eumorfopoulos, *Phil. Mag.*, 1898, 41, 360; Schenck and Rassbach, *ibid.*, 1907, 40, 2185, 2947; 1908, 41, 2917.

a transition point at 850° C. The molecular heat of formation of lead sulphate from its elements is 216,200 calories<sup>1</sup>; the following are the heats of formation in other ways:



Lead sulphate is not quite insoluble in water; at atmospheric temperature 1 part of the salt dissolves in about 22,000 parts of water. Dibbitts<sup>2</sup> found that 1 litre of water dissolves 0.038 gram  $\text{PbSO}_4$ ; but Schmal<sup>3</sup> found 0.0824 gram. The electric conductivities of aqueous solutions of lead sulphate at different temperatures ( $t_p$ ) have been measured by Kohlrausch,<sup>4</sup> and the corresponding solubilities deduced therefrom:

Temperature °C . . . . .	0.37	3.48	16.98	48.00	33.23
$\kappa \times 10^6$ . . . . .	16.73	19.57	34.82	32.4	48.5
Millimols. per litre . . . . .	0.110	0.117	0.131	0.131	0.114

Applying the same principle, but reckoning the salt to be 82 per cent. ionised, Böttger<sup>5</sup> has calculated the solubility of lead sulphate in water at 19.95° C. to be  $4.21 \times 10^{-2}$  gram per litre, a result which agrees closely with that of Kohlrausch. It has been pointed out, however, by Pleissner,<sup>6</sup> that not only does the question of degree of ionisation enter into the calculation of solubility from conductivity data, but also that of hydrolysis. These authors have estimated the state of an aqueous solution of lead sulphate at 18° C. to be as follows:

$[\text{PbSO}_4]$	0.027 millimols. per litre
$[\text{SO}_4^{''}]$	0.099 .. ..
$[\text{Pb}^+]$	0.062 .. ..
$[\text{Pb}(\text{OH})^+]$	0.037 .. ..
$[\text{H}^+]$	0.037 .. ..
Solubility product $[\text{Pb}^+] \times [\text{SO}_4^{''}]$	$61 \times 10^{-10}$ .

The solubility of lead sulphate is considerably less in dilute sulphuric acid than in water, but beyond a certain strength of acid the solubility again increases owing to the formation of complex ions. This is shown by the following figures:

Percentage $\text{H}_2\text{SO}_4$ . . . . .	0	1	29	64	86	99
Grams $\text{PbSO}_4$ per litre . . . . .	0.016	0.027	0.012	0.016	0.197	0.72

The solubilities of lead sulphate in hydrochloric acid of different concentrations at atmospheric temperature are as follow:<sup>7</sup>

Grams HCl per 100 grams solution . . . . .	10.6	16.3	22.0	27.5	31.6
Grams $\text{PbSO}_4$ per 100 grams solvent . . . . .	0.14	0.35	0.95	2.11	2.80

and in nitric acid, also at atmospheric temperature:

Grams $\text{HNO}_3$ per 100 grams solution . . . . .	11.6	17.5	34.0	60.0
Grams $\text{PbSO}_4$ per 100 grams solvent . . . . .	0.33	0.59	0.78	1.01

<sup>1</sup> Thomsen, *J. prakt. Chem.*, 1875, [ii], 12, 96

<sup>2</sup> Dibbitts, *Zeitsch. anal. Chem.*, 1874, 13, 139

<sup>3</sup> Schmal, *Compt. rend.*, 1900, 148, 1394

<sup>4</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 129

<sup>5</sup> Böttger, *Zeitsch. physikal. Chem.*, 1901, 46, 604

<sup>6</sup> Pleissner, *Archiv u. Kaiserl. Gesundheitsamte.*, 1907, 26, 384; *Chem. Zentr.*, 1907, ii, 1035

<sup>7</sup> Schultz, see Seidell, *Solubilities of Inorganic and Organic Substances* (Crosby Lockwood and Son, 1911), Rodwell, *J. Chem. Soc.*, 1882, 15, 50

\* Since ammonium acetate solution is used as a solvent for lead sulphate in qualitative analysis, the extent of its solvent action is of practical importance.

The following values have been obtained :

Temperature <sup>1</sup> 25° C.

Grams $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ per litre . . . . .	7.98	15.96	31.92
Grams $\text{PbSO}_4$ per litre . . . . .	0.636	1.38	3.02

Temperature <sup>2</sup> 100° C.

Grams $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ per litre . . . . .	280	320	370	450
Grams $\text{PbSO}_4$ per litre . . . . .	71.2	98.8	105.8	111.0

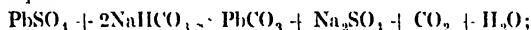
It has been shown by Fox <sup>3</sup> that with solutions of ammonium acetate up to a concentration of 3N the solid phase consists of lead sulphate, but with more concentrated solutions this phase consisted of crystals of  $(\text{NH}_4)_2\text{Pb}(\text{SO}_4)_2$ .

When lead sulphate dissolves in sodium acetate solution the solid phase consists of  $\text{PbSO}_4$ , but when it dissolves in potassium acetate there is double decomposition with the formation of lead acetate and potassium sulphate, the latter uniting with the lead sulphate to form the complex sulphate  $\text{K}_2\text{Pb}(\text{SO}_4)_2$  as the solid phase.<sup>4</sup>

Numerous other salts also increase the solubility of lead sulphate in water, prominent among which are ammonium nitrate, citrate, and tartrate.

Ethyl alcohol diminishes the solubility of lead sulphate, which is practically insoluble in pure alcohol; hence alcohol is added in order completely to separate lead as sulphate in qualitative and quantitative analysis.

Lead sulphate reacts with sodium hydrogen carbonate according to the equation :



whence it follows that carbon dioxide under pressure transforms lead carbonate suspended in sodium sulphate solution into lead sulphate.<sup>5</sup>

**Basic Lead Sulphates.**—By an investigation of the cooling curves of various fused mixtures of lead sulphate and monoxide Schenck and Rassbach <sup>6</sup> have found evidence of the existence of three basic lead sulphates, viz.  $\text{PbSO}_4 \cdot \text{PbO}$ ,  $\text{PbSO}_4 \cdot 2\text{PbO}$ ,  $\text{PbSO}_4 \cdot 3\text{PbO}$ , the first of which is the best defined.

$\text{PbSO}_4 \cdot \text{PbO}$  or  $\text{Pb}_2\text{OSO}_4$  is formed by the action of ammonia on lead sulphate,<sup>7</sup> and by shaking together lead sulphate and lead hydroxide with water at 18° C.<sup>8</sup> It is obtained as a white, voluminous powder, and occurs as the mineral *lanarkite*.  $\text{PbSO}_4 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$  or  $\text{Pb}_4\text{O}_5(\text{OH})_2\text{SO}_4$  is formed by the interaction of lead hydroxide and ammonium sulphate solution,<sup>9</sup> or by shaking lead sulphate and lead hydroxide with water.<sup>8</sup>

<sup>1</sup> Noyes and Whitecomb, *J. Amer. Chem. Soc.*, 1905, 27, 758.

<sup>2</sup> Dunnington and Long, *Amer. Chem. J.*, 1899, 22, 217.

<sup>3</sup> Fox, *Proc. Chem. Soc.*, 1907, 23, 200.

<sup>4</sup> Fox, *Trans. Chem. Soc.*, 1909, 95, 878; see also Brönsted, *Zetsch. physikal. Chem.*, 1911, 77, 315; and Blomberg, *Chem. Weekblad*, 1914, 11, 1030.

<sup>5</sup> Auerbach and Pick, *Arbeiten Kaiserl. Gesundheitsamts*, 1913, 45, 113.

<sup>6</sup> Schenck and Rassbach, *Ber.*, 1908, 41, 2917.

<sup>7</sup> Kuhn, *Arch. Pharm.*, 1847, [ii], 50, 285; Strömholm, *Zeitsch. anorg. Chem.*, 1904, 38, 443.

<sup>8</sup> Pleissner, *Arbeiten Kaiserl. Gesundheitsamts*, 1907, 26, 384.

## LEAD AND ITS COMPOUNDS

According to Meissner 1 litre of saturated solution at 18° C. contains 18.4 mg. of  $\text{PbSO}_4 \cdot \text{PbO}$  and 26.2 mg. of  $\text{PbSO}_4 \cdot 8\text{PbO} \cdot \text{H}_2\text{O}$ .

A basic lead sulphate known to the trade under the name of *Purex* is made by volatilising galena in a current of air. The product constitutes a useful white pigment, much less poisonous than ordinary white lead.

**Lead Hydrogen Sulphate**,  $\text{PbH}_2(\text{SO}_4) \cdot \text{H}_2\text{O}$ .—Lead dissolves in hot and moderately concentrated sulphuric acid, in which also lead sulphate dissolves, forming an acid sulphate in solution. When this solution is diluted with water lead sulphate is precipitated, but if instead it is allowed to stand in the air crystals of the acid sulphate  $\text{Pb}(\text{HSO}_4)_2 \cdot \text{H}_2\text{O}$  are deposited.<sup>1</sup> Barium sulphate behaves similarly.

**Lead Pyrosulphate**,  $\text{PbS}_2\text{O}_7$ , is formed by the union of  $\text{PbSO}_4$  and  $\text{SO}_3$ .<sup>2</sup> It has not, however, been obtained pure.

**Plumbic Sulphate**, lead disulphate,  $\text{Pb}(\text{SO}_4)_2$ , is formed by the electrolytic oxidation of lead in presence of sulphuric acid. It was prepared by Elbs and Fischer<sup>3</sup> by the electrolysis of sulphuric acid of density 1.7 to 1.8 with a lead anode. The temperature did not exceed 30° C., the current density was 0.02 to 0.06 ampere per sq. cm., and the anode was separated from the cathode by immersion in a porous pot containing a considerable volume of the acid. The anode mud contained 60 to 85 per cent. of plumbic sulphate, a purer product subsequently crystallised from the anode liquid. The crystals of plumbic sulphate were of a faintly greenish yellow tint, but yielded a practically white powder when dried on a porous plate. They could not, however, be completely freed from sulphuric acid.

One hundred c.c. of sulphuric acid dissolve about 0.315 gram of plumbic sulphate at 30° C. This salt is hydrolysed by water into sulphuric acid and lead dioxide; the same effect is produced more slowly by the action of sulphuric acid of density less than 1.65. Hydrolysis, however, takes place in two stages,<sup>4</sup> the basic sulphate  $\text{PbOSO}_4 \cdot \text{H}_2\text{O}$  being an intermediate product.

Concentrated hydrochloric acid dissolves plumbic sulphate forming a yellow solution containing lead tetrachloride or chloroplumbic acid; glacial acetic acid also dissolves the salt at 40–50° C., and white needles of the tetra-acetate crystallise from the solution on cooling. Sodium acetate solution likewise dissolves plumbic sulphate, forming sodium plumbi-acetate, double salts, such as  $\text{K}_2\text{Pb}(\text{SO}_4)_3$  and  $(\text{NH}_4)_2\text{Pb}(\text{SO}_4)_3$ , are also formed with sulphates of the alkali metals, ammonia, and amines. Cold concentrated sodium hydroxide solution forms sodium plumbate.

Plumbic sulphate resembles, but is more energetic than, lead dioxide as an oxidising agent; ferrous salts are oxidised to ferric, alcohol to aldehyde, and oxalic acid to carbon dioxide by this compound. These oxidations are accompanied by the separation of lead sulphate, without the appearance of the dioxide.

**Lead Persulphate**,  $\text{PbS}_2\text{O}_8 \cdot (\frac{1}{2})3\text{H}_2\text{O}$ , is formed in solution by adding lead carbonate to persulphuric acid solution, and is obtained on evapora-

<sup>1</sup> Schultz *Pogg. Annalen*, 1865, 133, 137.

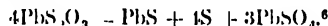
<sup>2</sup> Schultz, *Ber.*, 1884, 17, 2705.

<sup>3</sup> Elbs and Fischer, *Zetsch. Elektrochem.*, 1900, 7, 313.

<sup>4</sup> Dolozalek and Finckh, *Zetsch. anorg. Chem.*, 1908, 50, 82; 1907, 51, 320.

tion *in vacuo* in ill-defined, deliquescent crystals, very soluble in water.<sup>1</sup> From a solution of lead persulphate alkali precipitates lead hydroxide, which is quickly oxidised to the dioxide. It is noteworthy that this salt,  $\text{PbS}_2\text{O}_8$ , is isomeric with plumbic sulphate,  $\text{Pb}(\text{SO}_4)_2$ .

**Lead Thiosulphate**,  $\text{PbS}_2\text{O}_3$ , is formed as a white precipitate, which may be amorphous or crystalline, when sodium thiosulphate is added to a lead salt solution.<sup>2</sup> When heated it turns black, decomposing into lead sulphide and sulphate, together with sulphur and sulphur dioxide. It burns in the air; and when mixed with an oxidising agent has been employed in the manufacture of matches free from phosphorus. When sodium thiosulphate is added to a boiling solution of a lead salt containing ammonium chloride the whole of the lead is precipitated as sulphide,<sup>3</sup> together with free sulphur.<sup>4</sup> Lead thiosulphate is very slightly soluble in water; according to Rammelsberg,<sup>5</sup> 1 part dissolves in 8266 parts of water. Hot water decomposes this salt, producing sulphide, sulphate, and free sulphur, with small amounts of sulphuric acid, the main reaction being:



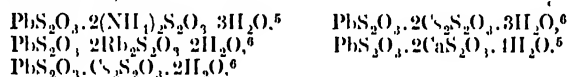
It is more soluble in thiosulphate solutions, owing to the formation of complex salts, a number of which are known.

$\text{PbS}_2\text{O}_3 \cdot \text{Li}_2\text{S}_2\text{O}_3$  is a crystalline salt which readily absorbs and is decomposed by water with formation of lead monosulphide.<sup>7</sup>

$\text{PbS}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3$ , obtained by adding lead acetate to concentrated sodium thiosulphate solution, is crystalline, and slightly soluble in water.<sup>8</sup>

$\text{PbS}_2\text{O}_3 \cdot 2\text{K}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  crystallises from a saturated solution of lead thiosulphate in potassium thiosulphate solution.<sup>5</sup>

The following salts also exist:



**Lead Dithionate**,  $\text{PbS}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , crystallises from a solution of lead carbonate in dithionic acid.<sup>9</sup> in stable, hexagonal crystals, isomorphous with the corresponding calcium and strontium salts. The tri- and tetra-thionates,  $\text{PbS}_3\text{O}_6$ <sup>10</sup> and  $\text{PbS}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ,<sup>11</sup> respectively are also known.

## LEAD AND SELENIUM

**Lead Selenide**,  $\text{PbSe}$ , occurs in nature as the rare mineral *claus-thalite*, and may be prepared by fusing the two elements together, or by precipitating a lead salt with hydrogen selenide. It may be obtained in a crystalline state by melting selenium with excess

<sup>1</sup> Marshall, *Trans. Chem. Soc.*, 1891, 59, 782.

<sup>2</sup> Letts, *Ber.*, 1870, 3, 922; Fogh, *Compt. rend.*, 1890, 110, 522, 571.

<sup>3</sup> Faktor, *Zeitsch. anal. Chem.*, 1900, 39, 345.

<sup>4</sup> Norton, *Chem. News*, 1901, 89, 254.

<sup>5</sup> Rammelsberg, *Pogg. Annalen*, 1842, 56, 308.

<sup>6</sup> Perkins and King, *Trans. Chem. Soc.*, 1913, 103, 300.

<sup>7</sup> Meyer and Fgeling, *Ber.*, 1907, 40, 1351.

<sup>8</sup> Wells and Walden, *Zeitsch. anorg. Chem.*, 1893, 3, 203.

<sup>9</sup> Heeren, *Pogg. Annalen*, 1826, 7, 171.

<sup>10</sup> Fogh, *Compt. rend.*, 1890, 110, 524.

<sup>11</sup> Fordos and Gélus, *Compt. rend.*, 1842, 15, 920; Kessler, *Pogg. Annalen*, 1848, 74, 249; Chancel and Diacon, *Compt. rend.*, 1863, 56, 710.

of lead, and dissolving away uncombined lead with nitric acid<sup>1</sup>; also by reducing lead selenate with carbon, by the interaction of hydrogen selenide and lead chloride vapour, or by fusing the precipitated sulphide in an electric furnace. Crystalline lead selenide is lustrous and bluish grey, and has a density of 8.10 at 15° C. It is slowly attacked by fuming hydrochloric acid, and more readily by nitric acid. The molecular heat of formation of amorphous lead selenide is 13,000 calories, and of the crystalline compound 15,800 calories.<sup>2</sup>

When lead is fused with excess of selenium, two layers are formed, the lower one of which contains nearly twice as much selenium as corresponds with the monoselenide, while the upper layer is nearly pure selenium. The monoselenide, however, is the only compound present in the lower layer, the excess of selenium being due to the solubility of the element in the fused monoselenide.<sup>3</sup>

**Lead Selenite**,  $\text{PbSeO}_3$ , is a white powder, sparingly soluble in water, prepared by decomposing a lead salt with selenous acid or a soluble selenite, by dissolving lead oxide in the same acid,<sup>4</sup> or by oxidising lead selenide with nitric acid<sup>5</sup>; it fuses without decomposition forming a yellow liquid.

**Lead Selenate**,  $\text{PbSeO}_4$ , was obtained by Berzelius as a white powder, difficultly soluble in water. When fused it evolves oxygen, and is reduced by hydrogen to selenide.<sup>6</sup> The basic salt  $\text{PbSeO}_3 \cdot 3\text{PbO} \cdot \text{H}_2\text{O}$  has been prepared from ammonium selenate and lead hydroxide.<sup>7</sup>

#### LEAD AND TELLURIUM

**Lead Telluride**,  $\text{PbTe}$ , occurs as the rare mineral *allatite*, which forms crystals in the regular system, of density 8.159 and hardness<sup>8</sup> 31.85 kg per sq. mm.<sup>9</sup> This compound can be prepared synthetically from its elements, and its molecular heat of formation is 11,400 calories.<sup>9</sup>

**Lead Tellurite**,  $\text{PbTeO}_3$ , was described by Berzelius,<sup>10</sup> and the hydrated salt  $3\text{PbTeO}_3 \cdot 2\text{H}_2\text{O}$  has been obtained by Lenher and Wolesensky.<sup>11</sup>

**Lead Tellurate**. Normal and basic salts were described by Berzelius.

#### LEAD AND NITROGEN

**Lead Azide** (*Lead Azonide*, *Lead Hydrazonate*),  $\text{Pb}(\text{N}_3)_2$ . This salt was prepared by Curtius<sup>12</sup> by precipitating sodium or ammonium azoimide solution with lead acetate. It is soluble in excess of the precipitant, practically insoluble in cold water, but somewhat soluble in boiling water, a litre of which dissolves about 0.5 gram. It crystal-

<sup>1</sup> Rosler, *Zeitsch. anorg. Chem.*, 1895, 9, 43.

<sup>2</sup> Fabre, *Ann. Chim. Phys.*, 1887, [vi], 10, 505.

<sup>3</sup> Pélabon, *Compt. rend.*, 1907, 144, 1159.

<sup>4</sup> Marino, *Zeitsch. anorg. Chem.*, 1908, 59, 150, 1909, 62, 173.

<sup>5</sup> Fonze-Diacon, *Bull. Soc. chim.*, 1900, [iii], 23, 721.

<sup>6</sup> Fonze-Diacon, *Compt. rend.*, 1900, 130, 1131.

<sup>7</sup> Stromholm, *Zeitsch. anorg. Chem.*, 1904, 38, 129.

<sup>8</sup> Saldau, *Ann. Inst. Minus, Petrograd*, 1913, 4, 228, see also Kimura, *Mem. Coll. Sci., Kyoto*, 1915, 8, 114.

<sup>9</sup> Fabre, *Ann. Chim. Phys.*, 1887, [vi], 10, 505.

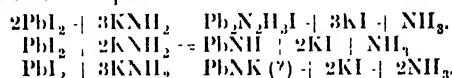
<sup>10</sup> Berzelius, *Lchbuch*, 1856, Bd. 3, 8, 749.

<sup>11</sup> Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1913, 35, 718.

<sup>12</sup> Curtius, *Ber.*, 1891, 24, 3341.

lises from aqueous solution in white needles which resemble lead chloride, but turn yellow in the light, and explode when heated. The salt dissolves in warm acetic acid, but not in ammonia. Hydrazoic acid is conveniently prepared by distillation when its lead salt is heated with dilute sulphuric acid.<sup>1</sup>

**Lead Imide, PbNH,** is one of the new compounds prepared by Franklin<sup>2</sup> by means of reactions carried out in liquid ammonia. When lead iodide reacts with potassiumide in liquid ammonia solution, the following reactions take place:



Lead imide may, however, be obtained by gradually adding lead iodide dissolved in liquid ammonia to a similar solution of potassiumide, until a considerable quantity is produced as an orange-coloured precipitate, which is then left in contact with the liquid for twenty-four hours. When dried, lead imide is a reddish brown, dense, amorphous mass, which is very explosive.

The product  $\text{Pb}_2\text{N}_2\text{H}_3\text{I}$ , which is formed when lead iodide is in excess, is white, and is called *ammono-basic lead iodide*; it may have the constitution represented by the formula  $\text{Pb} \cdot \text{N} \cdot \text{Pb} \cdot \text{I} \cdot \text{NH}_3$ , but more probably is  $\text{NH}_3 \cdot \text{Pb} \cdot \text{NH} \cdot \text{PbI}$ .

An *ammono-basic lead nitrate*, or lead *nitroso-nitride-ammonia*, to which the formula  $\text{Pb}_2\text{N}(\text{NO}) \cdot n\text{NH}_3$  has been attributed, is a white or pale yellow explosive compound formed by the action of potassiumide on lead nitrate in liquid ammonia solution.

**Lead Hyponitrite,  $\text{Pb}(\text{NO})_2$ ,** is formed by the interaction of sodium hyponitrite and lead acetate.<sup>3</sup> The first result of mixing the two solutions is the formation of a white precipitate; but this on standing in contact with acetic acid becomes yellow and crystalline.

The white salt is the basic hyponitrite  $\text{Pb}(\text{NO})_2 \cdot \text{PbO}$ ; the yellow crystalline salt is the pure hyponitrite  $\text{Pb}(\text{NO})_2$ . The former deflagrates when heated, the latter explodes. Both salts dissolve in dilute acids, and from the solution alkali precipitates the basic salt.

According to Divers,<sup>4</sup> however, freshly precipitated lead hyponitrite is cream-yellow, and is probably a hydrate, rather than a basic salt, which turns sulphur-yellow as it loses water.

The lead salt of *nitrohydroxyplumic acid*,  $\text{Pb}(\text{N}_2\text{O}_3)_2$ , is known.

**Lead Nitrites.** Besides normal lead nitrite numerous basic salts have been described, as well as a compound of nitrite and nitrate, formerly known as hyponitrate. These products have been obtained by the action of finely divided lead on a solution of lead nitrate or by the hydrolysis of lead nitrite. Lorenz<sup>5</sup> described fifteen of such compounds, and Peters<sup>6</sup> no less than twenty-eight. No doubt many of these supposed compounds were mixtures, and, therefore, it became an important and difficult problem to decide what individual compounds really exist. Our knowledge upon this subject is due largely

<sup>1</sup> Curtius and Russom, *J. prakt. Chem.*, 1898, [n], 58, 201.

<sup>2</sup> Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 821. *Zeitsch. anorg. Chem.*, 1905, 46, 27.

<sup>3</sup> Kirschner, *Zeitsch. anorg. Chem.*, 1894, 16, 428.

<sup>4</sup> Divers, *Trans. Chem. Soc.*, 1899, 85, 121.

<sup>5</sup> Lorenz, *Wien. Akad. Ber.*, 1857, 24, 1133.

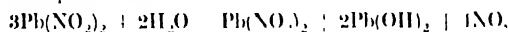
<sup>6</sup> Peters, *Zeitsch. anorg. Chem.*, 1896, 11, 116.

## LEAD AND ITS COMPOUNDS

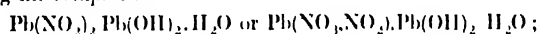
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to the work of Chilesotti,<sup>1</sup> who has given a résumé of the various lead nitrites which have been described, and submitted them to a critical examination.

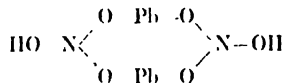
**Normal lead nitrite**,  $\text{Pb}(\text{NO}_2)_2$ , is prepared by mixing equivalent proportions of solutions of lead chloride and silver nitrite at 25° C., and concentrating the filtrate by freezing, followed by evaporation over sulphuric acid. The monohydrate  $\text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ <sup>2</sup> was thus obtained in yellow, transparent prisms, and subsequently the anhydrous salt  $\text{Pb}(\text{NO}_2)_2$ , mixed with a little lead oxide and nitrate. The electric conductivity of lead nitrite in concentrated solution is somewhat less than that of the nitrate or chloride, but on dilution the differences become small. It is probable, from their conductivity and their intense yellow colour, that solutions of lead nitrite contain complex anions of the type  $\text{Ag}(\text{NO}_2)_2^-$  or  $\text{Hg}(\text{NO}_2)_4^{2-}$ . Lead nitrite solution slowly decomposes thus:



a decomposition similar to that which nitrous acid itself undergoes; this reaction increases the conductivity of the solution. When a solution of lead nitrite is boiled and cooled, mucous scales are deposited, having the composition



and by further hydrolysis,  $3\text{PbO} \cdot \text{N}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  and  $4\text{PbO} \cdot \text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$  are produced. These three, together with the salt  $\text{Pb}(\text{NO}_2)_2 \cdot \text{Pb}(\text{OH})_2$ , are the only basic lead nitrites recognised by Chilesotti.  $\text{Pb}(\text{NO}_2)_2 \cdot \text{Pb}(\text{OH})_2$  may be regarded as a derivative of orthonitrous acid,  $\text{N}(\text{OH})_2$ , thus:



The existence of a nitrite-nitrate of lead has been investigated by Chilesotti by measurements of conductivity of mixed solutions of nitrite and nitrate. Owing to a change in the direction of the specific conductivity curve when the two salts are present in molecular proportions it is concluded that the two salts show some tendency to combine in the molecular ratio:  $\text{Pb}(\text{NO}_2)_2 : \text{Pb}(\text{NO}_3)_2$ . Attempts to separate a solid salt were, however, unsuccessful. Several double nitrites of lead and the alkali metals have been obtained.  $3\text{KNO}_2 \cdot 2\text{Pb}(\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$  crystallises in orange monoclinic crystals from a concentrated solution of lead acetate to which potassium nitrite has been added.<sup>3</sup>

$2\text{KNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ <sup>4</sup> is obtained when excess of  $\text{KNO}_2$  is added to lead acetate solution; according to Chilesotti, however, it is not pure, but mixed with the former salt.

$\text{CsNO}_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  forms bright orange plates.<sup>5</sup>

**Lead Nitrate**,  $\text{Pb}(\text{NO}_3)_2$ —Lead nitrate, or lead saltpetre, has long been known, and is mentioned in the *Alchymia* of Labavius by the name *calx plumbi dulcis*. It is obtained by dissolving lead, lead oxide, or

<sup>1</sup> Chilesotti, *Atti R. Accad. Lincei*, 1908, [v], 17, 1, 824; ii, 173, 288, 377, 474.

<sup>2</sup> Cf. Lang, *J. prakt. Chem.*, 1862, 86, 300.

<sup>3</sup> Fischer, *Pogg. Annalen*, 1847, 74, 115. Hampe, *Ann. Pharm.*, 1863, 125, 334.

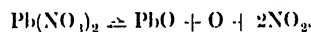
<sup>4</sup> Lang, *Jahresber.*, 1862, p. 102.

<sup>5</sup> Jamieson, *Amer. Chem. J.*, 1907, 38, 614.



lead carbonate in warm, dilute nitric acid, and crystallising the solution; commercially, lead scale or litharge is used for this purpose. The salt separates from aqueous solution in regular octahedra, in combinations of these forms with the cube, or in dodekahedra. Monoclinic crystals of lead nitrate have also been observed.<sup>1</sup> According to Hauser,<sup>2</sup> the form and transparency of the crystals depends upon the rate of cooling and degree of acidity of the solution. It was pointed out by Retgers<sup>3</sup> that crystals separated from an aqueous solution are porcelain-like, but that from a solution acidified by nitric acid they are clear; the explanation being that in the former case they are slightly basic owing to hydrolysis, whilst in the latter case they are pure.<sup>4</sup>

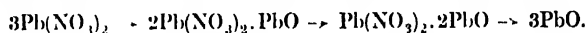
Lead nitrate has a density<sup>5</sup> of 4.531 at 24° C.; its refractive index<sup>6</sup> for sodium light at 20° C. is 1.7820; its molecular heat of formation from its elements is 105,500 calories.<sup>7</sup> Lead nitrate decrepitates when heated, detonates on red-hot charcoal, and deliquesces when rubbed with sulphur. The action of heat upon lead nitrate has been investigated by Backeland,<sup>8</sup> who finds that when the salt is heated to 357° C. in an evacuated and sealed glass tube, brown fumes are evolved, but are completely reabsorbed when the tube is cooled, according to the reaction



The connection between temperature and dissociation pressure was found to be as follows:

Temperature ° C.	223	230	250	274	296	357	448
Pressure mm. of mercury	6.2	6.9	11.8	32.6	78.4	514.0	1180.0

If, however, the salt is kept at 357° C. its power of evolving gas so as to regenerate the pressure after evacuation is much diminished, until the pressure attainable falls from 514 mm. to 260 mm. The residue is now slightly yellow and is a basic lead nitrate of the composition  $3\text{PbO} \cdot 2\text{N}_2\text{O}_5$  or  $2\text{Pb}(\text{NO}_3)_2 \cdot \text{PbO}$ . After the salt has been left at the same temperature in communication with the vacuum pump for ten days its dissociation pressure falls to zero, whilst its composition becomes  $3\text{PbO} \cdot \text{N}_2\text{O}_5$  or  $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{PbO}$ . This second basic salt loses all its nitrous fumes at a red heat, leaving a residue of oxide. So it is shown that lead nitrate is decomposed by heat in stages, thus:



The introduction of oxygen or nitrogen peroxide into the dissociation tube before the salt is heated, retards dissociation in accordance with the law of mass action. According to Colson,<sup>9</sup> perfectly dried lead nitrate shows no sign of decomposition in a vacuum till 288° C. is reached. On account of its decomposition, the melting-point of lead

<sup>1</sup> Morel, *Bull. Soc. Min.*, 1890, 13, 337.

<sup>2</sup> Hauser, *Wien Akad. Ber.*, 1860, 39, 139.

<sup>3</sup> Retgers, *Zeitsch. physikal. Chem.*, 1892, 9, 267.

<sup>4</sup> Lewis, *Dissertation Breslau*, 1908.

<sup>5</sup> Retgers, *Zeitsch. physikal. Chem.*, 1889, 4, 201.

<sup>6</sup> Leblanc and Roland, *Zeitsch. physikal. Chem.*, 1896, 19, 277.

<sup>7</sup> Thomsen, *Thermochemische Untersuchungen*, 1883, iii, 337. *J. prakt. Chem.*, 1875, [ii], 12, 96.

<sup>8</sup> Backeland, *J. Amer. Chem. Soc.*, 1904, 26, 391.

<sup>9</sup> Colson, *Compt. rend.*, 1909, 148, 837.

ate is unknown. This salt dissolves readily in water; the following solubility table includes the results of Mulder,<sup>1</sup> Kremers,<sup>2</sup> Michel and Kraft,<sup>3</sup> and Euler.<sup>4</sup>

Temperature (°C)	Grams $\text{Pb}(\text{NO}_3)_2$ per 1000 grams of		
	Water		Solution
	Mulder	Kremers	Michel and Kraft
0°	36.5	38.8	27.33
10	44.1	48.3	31.6
17	50.0	54.0	34.2
20	52.3	56.5	35.2
25	56.1	60.6	36.9
30	60.7	66.0	38.8
40°	69.1	75.0	41.9
50°	78.7	85.0	45.0
60°	88.0	95.0	47.8
80°	107.6	115.0	52.7
100°	127.0	138.8	57.1
	Euler		Euler
17°	52.76		34.54

The density of a saturated solution at 17° C. is 1.405 (Euler), and at 25.3° C. compared with water at the same temperature <sup>5</sup> 1.158.

The solubility of lead nitrate in water is much diminished by the addition of nitric acid, so that its aqueous solution is precipitated by concentrated nitric acid. The following figures show the influence of nitric acid on this solubility <sup>6</sup> at 25° C.:

Mols. $\text{HNO}_3$ per litre	0	2.02	4.64	8.77	14.35
Mols. $\text{Pb}(\text{NO}_3)_2$ per litre	1.63	0.536	0.187	0.042	0.0017

The densities of lead nitrate solutions of various strengths are as follow:

Per cent $\text{Pb}(\text{NO}_3)_2$	5	10	15	20	25	30	35
Relative densities <sup>7</sup> at 15° C.	1.015	1.095	1.147	1.204	1.268	1.336	--
(water at 4° C. = 1)							
Relative densities <sup>8</sup> at 17.5° C.	1.040	1.092	1.111	1.200	1.263	1.333	1.400
(water at 17.5° C. = 1)							

The solution of lead nitrate in water is accompanied by lowering of temperature; the heat of solution of 1 molecule  $\text{Pb}(\text{NO}_3)_2$  in 400

<sup>1</sup> Mulder, *Scheikundige Verhandelingen en Onderzoeksen*, Rotterdam, 1864, 66.

<sup>2</sup> Kremers, *Pogg. Annalen*, 1851, 92, 497.

<sup>3</sup> Michel and Kraft, *Ann. Chim. Phys.*, 1854, [4], 41, 471.

<sup>4</sup> Euler, *Zeitsch. physikal. Chem.*, 1901, 49, 314.

<sup>5</sup> Lewis, *Dissertation*, Breslau, 1908.

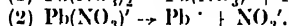
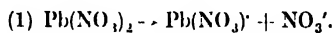
<sup>6</sup> Cumming, *Zeitsch. Elektrochem.*, 1907, 13, 19, 40.

<sup>7</sup> Long, *Wied. Annalen*, 1880, 11, 37.

<sup>8</sup> Gerlach, *Zeitsch. anal. Chem.*, 1888, 27, 271.

molecules of water is — 7,600 calories,<sup>1</sup> and of 1 molecule in 980–1860 molecules of water — 8,200 calories.<sup>2</sup>

From numerous estimations of depressions of freezing-point and conductivities of solutions of lead nitrate of various concentrations it is concluded that this salt is not appreciably hydrolysed at 25° C., but undergoes ionisation in two stages, thus<sup>3</sup>:



The extent of ionisation at 25.3° C. has been estimated by Lewis,<sup>4</sup> with the following results:

Mol. $\text{Pb}(\text{NO}_3)_2$ per litre	1	0.1	0.25	0.05	0.01
Concentration $\text{Pb}^{++}$ ions	0.0503	0.0408	0.0354	0.0168	0.0054
Percentage ionisation	5	10	14	34	54

Warm solutions of lead nitrate are appreciably hydrolysed. Thus Walker and Aston<sup>5</sup> estimated, by measurement of the inversion of cane-sugar, that a  $\frac{N}{2}$  solution of this salt is hydrolysed to 0.15 per cent. at 60° C.; Long,<sup>6</sup> however, found only 0.1 per cent. hydrolysis of a similar solution at 85° C.

The solubilities of lead nitrate in aqueous and absolute ethyl alcohol and in methyl alcohol are as follow:

Solvent.	Grams $\text{Pb}(\text{NO}_3)_2$ per 1000 grams solvent at				
	4° C.	8° C.	22° C.	40° C.	50° C.
Aqueous ethyl alcohol <sup>7</sup> (density 0.9282)	4.96	5.82	8.77	12.8	14.9
Absolute ethyl alcohol <sup>8</sup>			0.04 (20.5° C.)	—	—
Absolute methyl alcohol <sup>9</sup>			1.37	—	—

Lead nitrate has an astringent taste. It is used in calico printing, as a mordant in dyeing, and for the manufacture of chrome yellow.

**Basic Lead Nitrates.**—Various basic lead nitrates have been described. They are obtained by the action of metallic lead, lead oxide, white lead, potassium hydroxide, ammonia, or certain basic oxides on lead nitrate solution, or by dissolving lead oxide in solutions of other metallic nitrates; i.e. either by adding hydroxide ions to lead nitrate or nitrate ions to lead hydroxide.

<sup>1</sup> Thomsen, *J. prakt. Chem.*, 1875, [n], 12, 87; 1878, [n], 17, 177.

<sup>2</sup> Berthelot, *Ann. Chim. Phys.*, 1875, [v], 4, 101.

<sup>3</sup> Hausrath, *Ann. Physik.*, 1902, [iv], 9, 543; von Ende, *Zeitsch. anorg. Chem.*, 1903, 162; Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, 6, 386; Franke, *Zeitsch. physikal. Chem.*, 1895, 16, 463; Jagor, *Zeitsch. physikal. Chem.*, 1888, 2, 42; Kohlrausch and Gruneisen, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1215.

<sup>4</sup> Lewis, *Dissertation*, Breslau, 1903.

<sup>5</sup> Walker and Aston, *Trans. Chem. Soc.*, 1895, 67; 579.

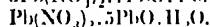
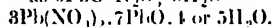
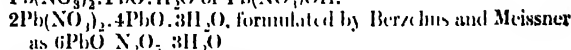
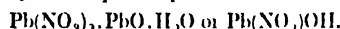
<sup>6</sup> Long, *J. Amer. Chem. Soc.*, 1896, 18, 693.

<sup>7</sup> Gerardin, *Ann. Chim. Phys.*, 1865, [iv], 5, 129.

<sup>8</sup> Lobry de Bruyn, *Zeitsch. physikal. Chem.*, 1892, 10, 783.

## LEAD AND ITS COMPOUNDS

The following salts appear to exist; other products which have been described are probably mixtures.<sup>1</sup>

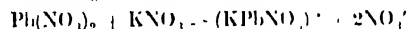


$\text{Pb}(\text{NO}_3)\text{OH}$  is prepared by boiling the normal salt with an equal weight of lead oxide and water, and cooling, when it separates in crystals, which are sparingly soluble in cold but more readily soluble in hot water. Carbon dioxide forms carbonate and the normal salt; gentle heat converts the compound into red lead.

The other salts are obtained by the action of lead hydroxide on potassium nitrate solution, or of ammonia on lead nitrate solution.

In addition to these, however, there are the two anhydrous basic salts formed during the careful ignition of solid lead nitrate,<sup>2</sup> viz.  $2\text{Pb}(\text{NO}_3)_2 \cdot \text{PbO}$  and  $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{PbO}$ .

A comparison of the solubilities of lead nitrate in water and in potassium and sodium nitrate solutions, as well as a study of the freezing-points of the simple and mixed solutions, leads to the conclusion that lead nitrate combines with alkali nitrates in solution to form complex ions, such as  $(\text{K}\text{Pb}\text{NO}_3)^+$ , so that a reaction, such as



takes place in solution.<sup>3</sup>

Lead nitrate forms with thionic the compounds<sup>4</sup>



and with pyridine  $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ,<sup>5</sup> and  $\text{Pb}(\text{NO}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N}$ .<sup>6</sup>

## LEAD AND PHOSPHORUS

A supposed allotropic form of phosphorus, known as "Hittorf's phosphorus," is obtained in a crystalline condition by the prolonged heating of phosphorus with lead. It has been shown by Luick and Möller<sup>7</sup> that this substance may contain as much as half its weight of lead. Nevertheless there is no evidence of the formation of a definite phosphide of lead in this way. By precipitating a solution of lead nitrate in liquid ammonia with a corresponding solution of rubidium phosphide,  $\text{Rb}_2\text{P}_2$ , **lead phosphide** is formed as a readily oxidisable black precipitate, having the composition  $\text{PbP}_2$ . When this compound is heated in a vacuum it loses all its phosphorus; it burns spontaneously in the air, is slowly attacked by water, gives solid hydrogen phosphide and lead salt with dilute acid, but with dilute nitric acid yields lead nitrate and phosphonic acid.<sup>8</sup>

<sup>1</sup> Wakeman and Wells, *Amer. Chem. J.*, 1887, 9, 299; Stromholm, *Zeitsch. anorg. Chem.*, 1904, 38, 444.

<sup>2</sup> Backlund, *J. Amer. Chem. Soc.*, 1901, 23, 391.

<sup>3</sup> Noyes, *Zeitsch. physikal. Chem.*, 1889, 6, 372; Löwig, *Dissertation*, Breslau, 1908.

<sup>4</sup> Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1906, 49, 18.

<sup>5</sup> Pincussohn, *Zeitsch. anorg. Chem.*, 1897, 14, 379.

<sup>6</sup> Werner, *Zeitsch. anorg. Chem.*, 1897, 15, 21.

<sup>7</sup> Luick and Möller, *Ber.*, 1908, 41, 1404.

<sup>8</sup> Bossuet and Hackspill, *Compt. rend.*, 1913, 157, 720.

**Lead Hypophosphite**,  $\text{Pb}(\text{H}_2\text{PO}_2)_2$ , is obtained by dissolving lead oxide or carbonate in aqueous hypophosphorous acid, and crystallising the solution. The salt forms leaflets or rhombic prisms, and is much more soluble in hot water than cold. Like other hypophosphites, it evolves spontaneously inflammable phosphine when heated, and leaves a residue of phosphate.<sup>1</sup>

**Lead Phosphite**,  $\text{PbHPO}_3$ , is a white powder obtained by precipitating a lead salt solution by a soluble phosphite, or by neutralising phosphorous acid with lead carbonate.<sup>2</sup> When heated it is converted into phosphine and phosphate. Its heat of formation from its elements is 227,700 calories. The acid salt  $\text{Pb}(\text{H}_2\text{PO}_3)_2$  is obtained by dissolving  $\text{PbHPO}_3$  in phosphorous acid, and by ignition in a vacuum yields the pyrophosphite  $\text{PbH}_2\text{P}_2\text{O}_5$ .<sup>2</sup> A basic phosphite exists which is  $3\text{PbO} \cdot \text{P}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  or  $4\text{PbO} \cdot \text{P}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .<sup>3</sup>

**Lead Orthophosphate**,  $\text{Pb}_3(\text{PO}_4)_2$ .—The normal salt is precipitated by adding a dilute acetic acid solution of lead acetate to excess of a boiling solution of sodium hydrogen phosphate.<sup>4</sup> If the precipitation takes place in the cold  $\text{PbHPO}_4$  is formed, but is changed into the normal phosphate by lengthened boiling with water<sup>5</sup>; the latter salt is also slowly hydrolysed by boiling water.<sup>6</sup> Lead phosphate is a yellow, amorphous powder, whose solubility in water amounts to  $1.66 \times 10^{-7}$  molecule per litre. It dissolves in caustic alkali solution.

**Lead Monohydrogen Phosphate**,  $\text{PbHPO}_4$ , is formed by adding phosphoric acid to boiling lead nitrate solution, and by heating lead pyrophosphate with water to  $250^\circ \text{C}$ .<sup>7</sup> It forms monoclinic prisms, very slightly soluble in water, having a density of 5.661. The salts  $\text{PbKPO}_4$  and  $\text{PbNaPO}_4$  are formed by heating lead oxide with potassium and sodium pyrophosphates.

**Lead Dihydrogen Phosphate**,  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ , is obtained by dissolving  $\text{PbHPO}_4$  in hot 90 per cent. phosphoric acid, and crystallising the solution. It forms fine needles which are hydrolysed by water (Alders and Stahler).

The basic salt  $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbO}$  is formed by heating the double salt  $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

The salt  $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$  occurs naturally as *pyromorphite* and can be prepared artificially by heating its constituent salts together.<sup>8</sup> It forms yellow, hexagonal crystals of density 7.008. The hydrate  $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}$  has also been prepared,<sup>9</sup> as well as the salts  $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbBr}_2$ <sup>10</sup> and  $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbI}_2$ .<sup>11</sup>

The crystalline compound  $2\text{Pb}(\text{HPO}_4)_2 \cdot \text{Pb}(\text{NO}_3)_2$  is formed by the evaporation of a solution of  $\text{Pb}_3(\text{PO}_4)_2$  in nitric acid<sup>12</sup>; and

<sup>1</sup> H. Rose, *Pogg. Annalen*, 1828, 12, 288; Wurtz, *Ann. Chim. Phys.*, 1855, [iii], 43, 327.

<sup>2</sup> H. Rose, *Pogg. Annalen*, 1827, 9, 42, 221; Rammeisberg, *Annalen*, 1867, 132, 489; Amat, *Compt. rend.*, 1890, 110, 901.

<sup>3</sup> Wurtz, *Ann. Chim. Phys.*, 1846, [iii], 16, 214.

<sup>4</sup> Mitscherlich, *Ann. Chim. Phys.*, 1821, 19, 359; Heintz, *Pogg. Annalen*, 1848, 73, 122.

<sup>5</sup> Alders and Stahler, *Ber.*, 1909, 42, 2261.

<sup>6</sup> Caven and Hill, *J. Soc. Chem. Ind.*, 1897, 16, 29.

<sup>7</sup> A. de Schulten, *Bull. Soc. franç. Minéral.*, 1904, 27, 109; Alders and Stahler, *ibid.*

<sup>8</sup> Manross, *Annalen*, 1852, 82, 348; Dobray, *Ann. Chim. Phys.*, 1861, [iii], 61, 419.

<sup>9</sup> Heintz, *Pogg. Annalen*, 1848, 73, 122.

<sup>10</sup> Ditte, *Compt. rend.*, 1883, 96, 846, 1227.

<sup>11</sup> Ditte, *Ann. Chim. Phys.*, 1886, [vi], 8, 532.

<sup>12</sup> Berzelius, *Ann. Chim. Phys.*, 1816, 2, 161.

$\text{Pb}_3(\text{PO}_4)_2 \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  is precipitated when an insufficiency of sodium phosphate is added to lead nitrate solution. The latter may be crystallised from nitric acid and yields the basic salt  $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbO}$  on ignition.<sup>1</sup>

**Lead Pyrophosphate**,  $\text{Pb}_2\text{P}_2\text{O}_7$ , is precipitated as a white, amorphous powder when a solution of a pyrophosphate is added to a lead salt solution<sup>2</sup>; and is also obtained when lead oxide is fused with potassium metaphosphate and the melt is extracted with water.<sup>3</sup> Water-vapour at  $280^\circ\text{--}300^\circ\text{C}$ . converts it into orthophosphate.<sup>4</sup> Various hydrates and double salts of lead pyrophosphate have been described. It is noteworthy that this salt shows so little tendency to pass into orthophosphate. A hydrate of sodium pyrophosphate would probably be impossible.

**Lead Metaphosphate.**—The lead metaphosphates appear first to have been investigated by Fleitmann and Henneberg,<sup>5</sup> who described two salts: the “dimetaphosphate”  $\text{Pb}_2\text{P}_4\text{O}_{12}$ , and the “trimetaphosphate”  $\text{Pb}_3\text{P}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$ . The subject was further investigated by von Knorre,<sup>6</sup> and later by Warschauer,<sup>7</sup> who has reached the following conclusions:

Two forms of lead metaphosphate can be produced, which are the same as those described by Fleitmann and Henneberg.

The first is obtained by heating the residue formed by evaporating the solution of a lead salt in excess of phosphoric acid to a temperature not exceeding  $100^\circ\text{C}$ . It consists of small shining needles which are distinctly soluble in water, and is identical with Fleitmann’s dimetaphosphate  $\text{Pb}_2\text{P}_4\text{O}_{12}$ . Warschauer, however, regards it as lead tetrametaphosphate, derived from tetrametaphosphoric acid,  $\text{H}_4\text{P}_4\text{O}_{12}$ .

The second salt is obtained by heating the same residue above  $400^\circ\text{C}$ . so as to fuse it, and then allowing it to cool slowly, so as to become crystalline. It is identical with Fleitmann’s trimetaphosphate, but is regarded as the lead salt of hexametaphosphoric acid,  $\text{H}_6\text{P}_6\text{O}_{18}$ . The identity of these salts was established by decomposing them with sodium sulphide, so as to obtain the corresponding sodium salts.

The cooling curves of fused mixtures of phosphoric oxide and lead oxide have been studied by Kroll<sup>8</sup>; and thus the existence of the following salts has been shown: the pyrophosphate  $2\text{PbO} \cdot \text{P}_2\text{O}_5$ , the “anorthophosphate”  $5\text{PbO} \cdot 2\text{P}_2\text{O}_5$ , the orthophosphate  $3\text{PbO} \cdot \text{P}_2\text{O}_5$ , the tetraphosphate  $4\text{PbO} \cdot \text{P}_2\text{O}_5$ , the octaphosphate  $8\text{PbO} \cdot \text{P}_2\text{O}_5$ .

## LEAD AND ARSENIC

The freezing-point curve of a mixture of lead and arsenic has been examined by Heycock and Neville,<sup>9</sup> and also by Descamps,<sup>10</sup> who was of opinion that lead forms several compounds with arsenic. Friedrich,<sup>11</sup>

<sup>1</sup> Gerhardt, *Annalen*, 1849, 72, 85.

<sup>2</sup> Gerhardt, *Ann Chem Phys*, 1848 [m], 22, 505.

<sup>3</sup> Ouvrard, *Compt. rend.*, 1890, 110, 1333.

<sup>4</sup> Reynoso, *Compt. rend.*, 1852, 34, 795.

<sup>5</sup> Fleitmann and Henneberg, *Annalen*, 1848, 65, 201; Fleitmann, *Pogg. Annalen*, 1849, 78, 253, 353.

<sup>6</sup> Von Knorre, *Zeitsch. anorg. Chem.*, 1900, 24, 369.

<sup>7</sup> Warschauer, *Zeitsch. anorg. Chem.*, 1903, 36, 137.

<sup>8</sup> Kroll, *Zeitsch. anorg. Chem.*, 1912, 78, 95; see also *Zeitsch. anorg. Chem.*, 1912, 77, 1.

<sup>9</sup> Heycock and Neville, *Chem. News*, 1891, 62, 280.

<sup>10</sup> Descamps, *Compt. rend.*, 1878, 86, 1022.

<sup>11</sup> Friedrich, *Metallurgie*, 1906, 3, 41.

however, who has prepared alloys of lead and arsenic containing 0 to 81.4 per cent. of arsenic, concludes that there is no evidence for the existence of any compound of the two elements.

**Lead Arsenite**,  $\text{Pb}_3(\text{AsO}_3)_2$ , is obtained as a white precipitate on adding an arsenite solution to an alkaline lead solution. When dried in the air, it becomes grey and black, which is attributed to the reduction of the lead to suboxide.<sup>1</sup> This salt is slightly soluble in water and easily soluble in caustic soda solution.

The pyroarsenite,  $2\text{PbO} \cdot \text{As}_2\text{O}_3$  or  $\text{Pb}_2\text{As}_2\text{O}_5$ , is a white powder formed by decomposing neutral lead acetate solution with ammoniacal arsenious oxide solution.<sup>1</sup> The pyroarsenite is also formed by the combination of arsenious oxide vapour with lead oxide.<sup>2</sup>

The metaarsenite  $\text{PbO} \cdot \text{As}_2\text{O}_3$  or  $\text{Pb}(\text{AsO}_2)_2$  is formed from a hot saturated solution of arsenious oxide in ammonia, and a neutral lead salt solution. It forms microscopic prisms, very slightly soluble in water.

**Lead Orthoarsenate**,  $\text{Pb}_3(\text{AsO}_4)_2$ , is precipitated as a white powder when ordinary sodium arsenate is added to lead acetate solution. When heated near its melting-point it turns yellow.<sup>3</sup>

**Lead Hydrogen Arsenate**,  $\text{PbHAsO}_4$ , is formed as a white, sparingly soluble, crystalline powder by the action of dilute nitric acid on the normal salt,<sup>4</sup> by the prolonged action of arsenic acid and air upon metallic lead, or by decomposing a lead nitrate solution with  $\text{Na}_2\text{HAsO}_4$ <sup>5</sup> or arsenic acid.

**Lead Pyroarsenate**,  $\text{Pb}_2\text{As}_2\text{O}_7$ , is obtained by precipitating lead acetate solution by sodium pyroarsenate,<sup>6</sup> and by fusing together lead oxide and potassium metaarsenate. In the latter case it forms colourless lamellae.

The mineral *minette* has the composition  $3\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{PbCl}_2$ . It may be prepared artificially by fusing its component salts together.<sup>6</sup>

## LEAD AND ANTIMONY

**Lead Antimonate.**—A white precipitate of lead metantimonate is formed when a solution of antimonie acid is added to one of lead acetate.<sup>7</sup> After drying in the air this precipitate has the composition  $\text{Pb}(\text{SbO}_3)_2 \cdot 9\text{H}_2\text{O}$ , but when dried over sulphuric acid it loses  $7\text{H}_2\text{O}$  leaving  $\text{Pb}(\text{SbO}_3)_2 \cdot 2\text{H}_2\text{O}$ , which may really be  $\text{PbHSbO}_4 \cdot \text{H}_2\text{SbO}_4$ . The pigment known as *Naples yellow* is an antimonate of lead containing excess of lead oxide. It is prepared by heating just to fusion for two hours 1 part of tartar emetic, 2 parts of lead nitrate, and 4 parts of sodium chloride (Brunner), or by heating 1 part of potassium antimonate with 2 parts of red lead (Guinnet). The product is washed with water, and a fine orange or yellow pigment results, which is employed in oil-painting and for staining glass and porcelain.

<sup>1</sup> Richard, *Ber.*, 1894, 27, 1019.

<sup>2</sup> Simon, *Pogg. Annalen*, 1837, 40, 411.

<sup>3</sup> Graham, *Pogg. Annalen*, 1834, 32, 51.

<sup>4</sup> Duvalier, *Be.*, 1876, 9, 189.

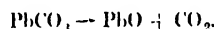
<sup>5</sup> Pickering, *Trans. Chem. Soc.*, 1907, 91, 310.

<sup>6</sup> Lechatelier, *Compt. rend.*, 1867, 65, 114.

<sup>7</sup> Senderos, *Bull. Soc. Chim.*, 1899, [in], 21, 57.

## LEAD AND CARBON

**Lead Carbonate,  $\text{PbCO}_3$ .**—The natural form of lead carbonate is *cerussite*, which occurs in rhombic crystals isomorphous with aragonite,  $\text{CaCO}_3$ ; strontianite,  $\text{SrCO}_3$ , and witherite,  $\text{BaCO}_3$ . Lead carbonate is also a constituent of *phosgenite*,  $\text{PbCO}_3 \cdot \text{PbCl}_2$ , and of *leadhillite*,  $2\text{PbCO}_3 \cdot \text{PbSO}_4 \cdot \text{Pb(OH)}_2$ . The normal salt may be prepared artificially by precipitating a cold solution of lead acetate or nitrate with ammonium carbonate, or by passing carbon dioxide into a dilute solution of lead acetate. If formed sufficiently slowly lead carbonate separates in the crystalline state.<sup>1</sup> It has been shown by Altmann,<sup>2</sup> however, that a basic carbonate of the composition of white lead  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$  may also be precipitated. Its formation is due to the previous hydrolysis of the lead acetate, which is promoted by dilution and raising the temperature, and especially by carrying out the reaction at 100° C. under a reflux condenser, so that vapourised acetic acid can escape. From lead nitrate solution carbonate is not precipitated by carbon dioxide. Crystallised lead carbonate<sup>3</sup> has a density of 6.17, that of the amorphous salt being 6.13. The molecular heat of formation of the crystallised salt from its elements is 169,500 calories (Thomsen<sup>4</sup>) or 166,700 calories (Berthelot<sup>5</sup>). Lead carbonate is dissociated by heat in the sense of the reaction:



According to Debray<sup>6</sup> the reaction is not reversible, but Colson<sup>7</sup> has shown that the white oxide formed by the decomposition of lead carbonate,  $\text{PbCO}_3$ , at as low a temperature as possible absorbs carbon dioxide readily, though the yellow oxide formed by heating the carbonate to 350° C. has not this property, probably because it is polymerised. Thus the reaction is reversible if the disturbance due to polymerisation is eliminated, and a little water-vapour has been found greatly to accelerate the establishment of equilibrium between lead carbonate and its dissociation products. The following are the dissociation pressures of lead carbonate when dry and also when moist:

Temperature ° C.	184	210	233	280	285
Dissociation Pressure, mm. Hg (dry)	10	32.5	102	518	760 <sup>8</sup>
Dissociation Pressure, mm. Hg (moist)	12	33	104	—	—

Lead carbonate is very slightly soluble in pure water; 1 litre of water dissolves 0.0011 to 0.0017 gram  $\text{PbCO}_3$ <sup>9</sup> at 20° C., according to measurements of electric conductivity. There is no hydrolysis below

<sup>1</sup> Frémy, *Compt. rend.*, 1866, 63, 714. Dreyer, *Annalen*, 1853, 87, 120.

<sup>2</sup> Altmann, *Zeitsch. anorg. Chem.*, 1907, 52, 219.

<sup>3</sup> See Falk, *Chem. Zeit.*, 1910, 34, 937.

<sup>4</sup> Thomsen, *J. prakt. Chem.*, 1860 [n.], 21, 44.

<sup>5</sup> Berthelot, *Ann. Chim. Phys.*, 1875, [5], 4, 176.

<sup>6</sup> Debray, *Compt. rend.*, 1878, 86, 511.

<sup>7</sup> Colson, *Compt. rend.*, 1906, 140, 865.

<sup>8</sup> Colson, *Compt. rend.*, 1909, 148, 837.

<sup>9</sup> Kohlrausch and Rose, *Zeitsch. physikal. Chem.*, 1893, 12, 241. Bottger, *Zeitsch. physikal. Chem.*, 1903, 46, 602.



76° C., but at that temperature the water begins to show an alkaline reaction; and if air free from carbon dioxide is drawn through the liquid so as to remove the liberated carbon dioxide, the carbonate is changed into the basic salt  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ .

Lead carbonate is much more soluble in water containing dissolved carbon dioxide than in pure water, as the following figures show (Pleissner<sup>1</sup>), *t* 18° C.:

Mgms. $\text{CO}_2$ per litre . .	0 0	2 8	5 1	14 4	26 0	43 5	106
Mgms. $\text{PbCO}_3$ per litre .	1 75	6 0	7 0	8 2	9 9	10 9	15 7

The interaction of lead carbonate and solutions of alkali carbonates has been investigated by Auerbach and Pick.<sup>2</sup>

#### BASIC LEAD CARBONATES

Various basic carbonates of lead have been described,<sup>3</sup> but only three are definitely known.  $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$  occurs as a mineral in Sweden and Scotland.  $4\text{PbCO}_3 \cdot 2\text{Pb(OH)}_2 \cdot \text{PbO}$  has been prepared by Stromholm<sup>4</sup> by the action of dilute sodium carbonate solution on lead hydroxide.

$2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , together with more or less normal carbonate, constitutes *white lead*. It is, therefore, the most important of the basic carbonates of lead, and the establishment of its chemical individuality is important.

This has been done by Hawley,<sup>5</sup> who left mixtures of lead oxide and carbonate in varying proportions in contact with 20 per cent. sodium acetate solution for twelve to fourteen hours. After this time the solid phase was found to contain a definite compound of the composition  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ . Salvadori<sup>6</sup> found, too, that when lead carbonate, precipitated from cold lead nitrate solution by ammonium carbonate, is boiled with water for some time, hydrolysis proceeds as far as a product having the composition  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ . The fact that the basic carbonate formed by the action of air and water on metallic lead possesses the same composition is additional evidence of the definite character of this compound. Euston,<sup>7</sup> nevertheless, believes that the basic carbonate is not a true compound, but an adsorption compound of lead carbonate and lead hydroxide.

**White Lead.**—This substance was known to Theophrastus, Pliny, and Dioscorides. Theophrastus describes its preparation by the action of vinegar on lead, and Pliny mentions the same process. The Latin Geber also gave an account of its manufacture by the action of the vapour of vinegar on lead; and until Bergmann, in 1774, showed that white lead is a compound of lead calx and fixed air, this substance was supposed to be a compound of the calx and vinegar.

White lead was known as *φαιίδιον* by Theophrastus, *cerussa* by Pliny, and *luft-sauer blei-kalk* by Bergmann.

<sup>1</sup> Pleissner, *Arbeiten Kaiserl. Gesundheitsamte*, 1907, 26, 384; *Chem. Zentr.*, 1907, ii, 1055.

<sup>2</sup> Auerbach and Pick, *Arbeiten Kaiserl. Gesundheitsamte*, 1913, 45, 113.

<sup>3</sup> Rose, *Pogg. Annalen*, 1851, 84, 52, 1853, 95, 284.

<sup>4</sup> Stromholm, *Zeitw. anorg. Chem.*, 1904, 38, 429.

<sup>5</sup> Hawley, *J. Physical Chem.*, 1906, 10, 654.

<sup>6</sup> Salvadori, *Gazzetta*, 1904, 34, i, 87.

<sup>7</sup> Euston, *J. Ind. Eng. Chem.*, 1914, 6, 202, 382.

Various processes have been employed for the manufacture of white lead.

1. *Dutch Stack Process*.—This is the oldest commercial process for the manufacture of white lead, and it is based upon the reaction which was known to the Ancients. Lead sheets, rolled into spirals, are lodged vertically upon three projections fixed at one-third of the way up conical, glazed earthenware pots, and are covered with lead plates, after the pots have been filled to one-fourth of their depth with vinegar. These pots are placed upon horse-dung in a shed, and by the use of boards are piled tier upon tier. Within four or five weeks the greater portion of the lead has been converted into white lead by chemical changes, the course of which is as follows: The fermentative oxidation of the dung liberates heat which vaporises the acetic acid; and this vapour, in conjunction with air, converts the lead into basic acetate. Meanwhile carbon dioxide has been generated by the fermentation of the dung, and this together with water-vapour acts upon the basic acetate, converting it into white lead or basic carbonate, and normal acetate. This latter by further action of carbon dioxide is changed into white lead with liberation of acetic acid; and the liberated acid then attacks fresh lead so that the process is repeated. The white lead is finally removed from any remaining "blue" or metallic lead, ground with water into a paste, washed so as to remove the soluble acetate, and then dried. The process of drying the lead pulp is attended by risk of poisoning to the workmen; and since the product is usually to be made into a paint, it is mixed with oil while wet, according to Ismay's process,<sup>1</sup> and agitated in a "pug mill," which separates most of the water, the remainder being eliminated by surrounding the mill with a heating jacket whilst a partial vacuum is maintained.

2. *English Stack Process*. This method differs from the Dutch method in the substitution of spent tannery bark for stable manure and dilute pyroigneous acid for vinegar. The lead also, instead of being in sheets, rolled into spirals, is cast into straps which are laid on the pots. At the end of the process, which is rather more lengthy than the Dutch process, the white lead, which preserves the shape of the strap, though the bulk has increased, presents a white, porcelain-like appearance; and when the mass is broken a thin core of lead is found within it. The product is now crushed and sieved, whereby the lead is flattened out and separated from the carbonate. After washing and drying the pigment is ready for the market. If the white lead shows a yellowish tint owing to staining from the bark, this is counteracted by the addition of a minute quantity of Prussian blue or indigo.

3. *Chamber Process*. The chemistry of this process is similar to that of the former processes, but the use of dung or tan is dispensed with. A usual continental practice is to hang thin straps of lead over a mixture of vinegar and wood-lice in boxes heated to 30° C., and then to introduce carbon dioxide. The process is quicker than the Dutch process, and the product consequently suffers somewhat in quality.

According to a patent process,<sup>2</sup> the fermentation gases escaping in the manufacture of spirits are employed for the manufacture of white lead. These gases contain water-vapour, carbon dioxide, and a little alcohol. They are driven by means of compressed air into a special

<sup>1</sup> Eng. Patent 23,909, 1895

<sup>2</sup> German Patent 151,514

chamber, where the alcohol is oxidised to acetic acid, and thence into the chambers containing the lead.

In Cookson's Chamber Process<sup>1</sup> straps of lead are suspended in a series of chambers, and all the necessary gases—carbon dioxide, oxygen, water-vapour, and acetic acid vapour—are generated separately and introduced into the chambers by means of pipes in the floors. Perfect control of both temperature and gases is obtained, and the product is very white, being entirely free from contamination with tan, etc., which so frequently occurs in the old stack process.

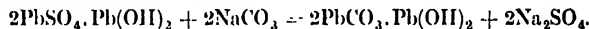
4. *French Method.*—According to this method, which was originated by Thénard, litharge is dissolved in pyroligneous acid of 1.056 density, basic lead acetate being produced in solution. Carbon dioxide is then forced through the solution by means of a fan; and this precipitates white lead, leaving neutral acetate in solution, which can afterwards be made to dissolve more litharge so that the process of carbonation may be repeated. This process has undergone several modifications.<sup>2</sup>

5. *American Method.*—Metallic lead in a molten condition is broken into fine spray which is brought together with acetic acid into rotating barrels.<sup>3</sup> Filtered combustion gases are blown with steam through the barrels for seven days, and the white lead thus produced is washed by means of water from the unchanged metal. The chemistry of the process is essentially the same as that of the preceding processes.

6. *Bronner's Method.*<sup>4</sup>—Freshly precipitated lead sulphate is warmed with caustic soda to 70° C., so that a basic sulphate is formed thus:



and when this product is warmed with sodium carbonate solution white lead is produced, thus:



7. *Milner's Method.*<sup>5</sup>—The process of Dale and Milner consisted in grinding litharge or any insoluble lead salt between millstones with water and sodium bicarbonate; but the Milner process introduced as an improvement consists in grinding together for three or four hours 4 parts of litharge, 1 part of common salt, and 16 parts of water. The mass gradually swells up and becomes white and pasty, there being produced a mixture of basic lead chloride and caustic soda. Carbon dioxide is then passed through the paste with constant stirring until its reaction to litmus is neutral, the basic chloride thus being converted into basic carbonate. Too much carbon dioxide would spoil the product. A somewhat similar process is that of Hof,<sup>6</sup> in which lead oxychloride, together with magnesium oxychloride, is produced by dissolving lead oxide in magnesium chloride solution. The former is then decomposed by carbon dioxide with the formation of white lead.

8. *Bischoff's Method.*—This process,<sup>7</sup> which is carried out at the works of Messrs. Mond at Brimsdown, Middlesex, consists in heating litharge to 250°–300° C. in a stream of water-gas, whereby it is reduced

<sup>1</sup> See *How White Lead is Manufactured*, by Cookson and Co., Newcastle, 1910.

<sup>2</sup> German Patent 133,425, Amer. Patent 750,541; German Patent 158,309.

<sup>3</sup> Winteler, *Zeitsch. angew. Chem.*, 1905, 18, 1179.

<sup>4</sup> German Patent 52,262.

<sup>5</sup> Eng. Patent 4053, 1875.

<sup>6</sup> Hof, *Chem. Zeit.*, 1900, 33, 1077; *Zeitsch. anorg. Chem.*, 1913, 81, 40.

<sup>7</sup> Caro, *Verh. Vereins Beförderung Gewerbleißes*, Berlin, 1906.

## LEAD AND ITS COMPOUNDS

to a black suboxide which is converted into a yellow hydroxide with water. Carbon dioxide then changes this hydroxide into white lead.

9. *Electrolytic Methods.*—The principle of these methods consists in producing lead hydroxide by electrolytic oxidation of metallic lead, which is then carbonated by the passage of carbon dioxide through the electrolytic cell. In a German process a 1.5 per cent. aqueous solution of 80 parts of sodium chlorate, and 20 parts of sodium carbonate, is electrolysed with an anode of soft lead, and a cathode of hard lead; the electrolyte is kept slightly alkaline, and carbon dioxide is passed through the solution.

In a French process<sup>1</sup> a 1 per cent. solution of sodium chloride is electrolysed with lead electrodes, whilst a current of carbon dioxide is passed through the solution to precipitate white lead from the alkali plumbite formed.

*Properties of White Lead.* White lead is an earthy, heavy, amorphous powder, which is seen under the microscope to consist of rounded or oval grains of diameter varying between 0.0001 and 0.0004 inch. This pigment is valued on account of its covering power, in which it much exceeds zinc white or baryta white; it is, however, rapidly blackened by hydrogen sulphide, and the product has the composition  $4\text{PbCO}_3 \cdot \text{PbS} \cdot \text{Pb(OH)}_2$ .<sup>2</sup>

The covering power depends upon the density; the greater the density, the smaller the amount of oil absorbed and the more opaque the pigment. The presence of lead hydroxide in the pigment has been found by experience to be essential and the nearer the composition of the white lead approximates to that of the basic carbonate  $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$  the better is its quality. When the composition approximates to that of the normal carbonate the pigment is useless. This is shown in the following figures:<sup>3</sup>

	PbO	CO <sub>2</sub>	H <sub>2</sub> O	
—	86.32	11.36	2.32	$2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$
1	86.80	11.16	2.00	Best quality
2	86.24	11.68	1.81	Seconds
3	86.03	12.28	1.68	Thirds still useful
4	84.69	14.10	0.93	Inferior
5	83.47	16.15	0.25	Useless
—	83.52	16.18		$\text{PbCO}_3$

*White Lead Substitutes.*—White lead is frequently mixed with the much cheaper heavy spar, or with gypsum. Certain mixtures of white lead and heavy spar are of technical importance. Thus *Venetian white* is a mixture of equal parts of white lead and barium sulphate, *Hamburg white* of 1 part of white lead and 2 of barium sulphate, whilst *Dutch white* consists of 1 part of white lead to 3 of barium sulphate.

Owing to the poisonous properties of white lead attempts are continually being made to utilise other lead salts for pigmentary purposes,

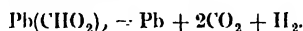
<sup>1</sup> French Patent 328,490.

<sup>2</sup> Socher, *Chem. Zeit.*, 1910, 34, 647.

<sup>3</sup> Weiss, *Monatsschr. Gewerbe-Vereins, Köln*; also *Dingler's polytech. J.*, 1873, 208, 434.

but hitherto with imperfect success, for the products do not possess quite the same "body" and smooth-working properties as genuine white lead. Thus *Pattinson's white lead* was the basic chloride  $\text{PbCl}_2 \cdot \text{Pb}(\text{OH})_2$ , the pigment *galenite* is a basic sulphate, and *Hannay's white lead* is the sulphate made from galena, which is said to possess considerable covering power.<sup>1</sup>

**Lead Formate**,  $\text{Pb}(\text{CHO}_2)_2$  or  $\text{Pb}(\text{OOC(H)})_2$ , is prepared by dissolving lead carbonate in formic acid solution, and readily crystallises in rhombic prisms<sup>2</sup> from the hot liquid. Anhydrous formic acid<sup>3</sup> is obtained from the crystals by decomposing them with hydrogen sulphide gas. When the dry salt is heated to  $190^\circ \text{C}$ . it decomposes thus<sup>4</sup>:



Lead formate shows considerable tendency to be hydrolysed in solution, and the following basic salts are formed by causing lead oxide to react with solutions of the normal formate under different conditions<sup>4</sup>:  $\text{Pb}(\text{CHO}_2)_2 \cdot \text{PbO}$ ;  $\text{Pb}(\text{CHO}_2)_2 \cdot 2\text{PbO}$ ;  $\text{Pb}(\text{CHO}_2)_2 \cdot 3\text{PbO}$ .

**Lead Acetate** (*Sugar of Lead*),  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ —This salt has been known for four or five hundred years. It is prepared by dissolving lead oxide in acetic acid, and is formed slowly by the action of acetic acid and air upon lead. The trihydrate forms monoclinic crystals,<sup>5</sup> isomorphous with those of barium and zinc acetates; it has a density of 2.50.<sup>6</sup> The hydrated salt easily loses water when gently heated, melts at  $75^\circ \text{C}$ ., and at  $100^\circ \text{C}$ . loses acetic acid as well as water, giving rise to a basic salt. The following are the aqueous vapour pressures of this salt at different temperatures<sup>7</sup>:

Temperature $^\circ \text{C}$ .	12.5	15.8	18.3	20.9	21.3	30.1
Vapour Pressure, mm. Hg.	2.92	4.29	5.32	6.81	7.14	14.91

The anhydrous salt has a density of 3.251, melts at  $280^\circ \text{C}$ ., and when strongly heated evolves first acetic acid vapour, then carbon dioxide and acetone, and finally leaves a residue of pyrophoric lead.<sup>8</sup>

If paper is soaked in lead acetate solution and dried, it smoulders like tinder when ignited. This may be due to the formation and combustion of pyrophoric lead.

The molecular heat of formation of the anhydrous salt is 232,600 calories.<sup>9</sup>

Lead acetate is readily soluble in water, and much more soluble in hot than in cold water; 100 grams of water dissolve 50 grams of the salt at  $25^\circ \text{C}$ ., 100 grams at  $40^\circ \text{C}$ ., and 200 grams at  $100^\circ \text{C}$ .<sup>10</sup>

The state of lead acetate in aqueous solution has been the subject of considerable investigation, as well as the cause of the solubility of lead sulphate in ammonium and sodium acetate solutions.

<sup>1</sup> See also *Purex*, p. 415.

<sup>2</sup> Heusser, *Jahresber.*, 1851, 434.

<sup>3</sup> Heintz, *Jahresber.*, 1856, 558.

<sup>4</sup> Barfüed, *J. prakt. Chem.*, 1869, 108, 1.

<sup>5</sup> Schroder, *Ber.*, 1881, 14, 1607.

<sup>6</sup> Buignet, *Jahresber.*, 1861, 15.

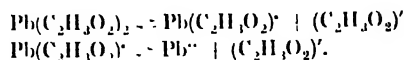
<sup>7</sup> Müller-Erbach, *Ber.*, 1887, 20, 2977.

<sup>8</sup> Wohler, *Annalen*, 1839, 29, 63.

<sup>9</sup> Thomson, *Thermochemische Untersuchungen*, 1882, i, 381.

<sup>10</sup> Oudemans, *Jahresber.*, 1868, 29; *Pharm. U.S.A.*, 1900.

So far as ionisation of lead acetate takes place, it probably occurs in two stages, as with other salts of lead and of other bivalent metals, thus<sup>1</sup>:

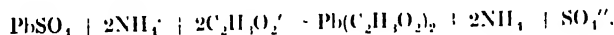


Noyes and Whitecomb<sup>2</sup> have found that lead acetate solution is, however, much less ionised than the acetates of barium, manganese, nickel, cobalt, zinc, and cadmium under equivalent conditions, and that, assuming dissociation into three ions, its degree of ionisation is only about 22 per cent. in decinormal solution.

This small degree of ionisation appears to be connected with the spontaneous formation of complex anions,<sup>3</sup> which occurs also with other acetates, and to a less extent with chlorides, sulphates, and nitrates.

The addition of an alkali acetate to lead acetate solution, by increasing the concentration of the acetate ions, increases the concentration of these complex anions; and this fact, as will appear, affords an explanation of the solubility of lead sulphate in acetate solutions. The solubilities of lead sulphate in ammonium acetate solutions of different strengths at 25° C. have been estimated by Noyes and Whitecomb<sup>2</sup> (see under Lead Sulphate, p. 444).

These same observers conclude that the lead is present in the acetate solution almost entirely in the non-ionised state, non-ionised lead acetate being formed by metathesis, thus



The solubility of lead sulphate in concentrated solutions of sodium and potassium acetates has been examined by Fox,<sup>4</sup> who concludes that metathesis takes place, according to the above equation, but that complex acetates are formed, such as  $\text{PbK}_2(\text{C}_2\text{H}_3\text{O}_2)_4$ , which probably would not exist in dilute solution, and that this salt, reacting with the potassium sulphate in solution, would produce the sparingly soluble salt  $\text{PbK}_2(\text{SO}_4)_2$ , which has been observed to crystallise.

Hydrated lead acetate dissolves in alcohol, 100 grams of alcohol dissolve 3.3 grams of the salt at 25° C. and 100 grams at 100° C.; 100 grams of glycerol dissolve 20 grams of lead acetate at 15° C.

Numerous *basic acetates* have been described, but probably only two are definite compounds.<sup>5</sup>

The salt  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$ , or  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$ , is formed when lead oxide is treated with excess of lead acetate solution, by the partial decomposition of the neutral acetate solution with ammonia or alkalis, or by dissolving the salt  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Pb}(\text{OH})_2$  in a solution of the normal acetate.

The salt  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Pb}(\text{OH})_2$  is formed by treating lead acetate solution with excess of lead oxide, or by pouring a solution of lead acetate into excess of ammonia.

<sup>1</sup> Jaques, *Trans. Faraday Soc.*, 1910, 5, 225.

<sup>2</sup> Noyes and Whitecomb, *J. Amer. Chem. Soc.*, 1905, 27, 747.

<sup>3</sup> Abegg and St. Laubenzin, *Zetsch. Elektrochem.*, 1904, 10, 77.

<sup>4</sup> Fox, *Trans. Chem. Soc.*, 1909, 95, 878.

<sup>5</sup> Lowe, *J. prakt. Chem.*, 1869, 98, 363.

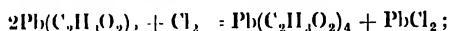
\* According to Sakabi,<sup>1</sup> the only solid compounds that can exist in contact with lead acetate solutions at 25° C. are :  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$ , and  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Pb}(\text{OH})_2$ .

**Complex Lead Acetates.**—Reference has already been made to the combination of lead acetate with alkali acetates in solution.<sup>2</sup> The double or complex acetate  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  was prepared by Rammelsberg,<sup>3</sup> and forms monoclinic crystals.

Various compounds of lead halides with lead and alkali acetates have been prepared.<sup>4</sup>

$\text{PbClC}_2\text{H}_3\text{O}_2$ ,  $5\text{PbIC}_2\text{H}_3\text{O}_2 \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  
 $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbCl}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $2(\text{PbIC}_2\text{H}_3\text{O}_2 \cdot \text{NaC}_2\text{H}_3\text{O}_2) \cdot \text{HC}_2\text{H}_3\text{O}_2$ ,  
 $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbCl}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{PbIC}_2\text{H}_3\text{O}_2 \cdot \text{KC}_2\text{H}_3\text{O}_2$ ,  
 $\text{PbClC}_2\text{H}_3\text{O}_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{PbIC}_2\text{H}_3\text{O}_2 \cdot \text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ .

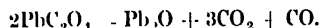
**Plumbic Acetate, Lead Tetra-acetate,**<sup>5</sup>  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ , is one of the most stable of the plumbic salts. It is obtained by dissolving red lead in warm, concentrated acetic acid. As the solution cools the tetra-acetate separates in white needles. It is also produced by the action of chlorine on a solution of the diacetate :



and is separated from the chloride formed simultaneously by means of warm acetic acid. The tetra-acetate melts at 175° C., is decomposed by water with the separation of lead dioxide, but is converted by hydrochloric acid into the tetrachloride. The following *organic salts of quadrivalent lead* have also been prepared<sup>6</sup> :

Plumbic propionate	: $\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_4$	
Plumbic <i>n</i> -butyrate	: $\text{Pb}(\text{C}_4\text{H}_7\text{O}_2)_4$	
Plumbic iso-butyrate	: $\text{Pb}(\text{C}_4\text{H}_7\text{O}_2)_4$	M.P. 109° C.
Plumbic palmitate	: $\text{Pb}(\text{C}_{16}\text{H}_{31}\text{O}_2)_4$	.. 88°-91° C.
Plumbic stearate	: $\text{Pb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_4$	.. 102°-103° C.

**Lead Oxalate,**  $\text{PbC}_2\text{O}_4$ , is obtained as a white precipitate when lead salt and oxalate solutions are mixed. When heated to 300° C. out of contact with air it decomposes according to the equation<sup>6</sup> :



Its solubility in water, determined by the conductivity method, is  $0.61 \times 10^{-5}$  gram-molecule per litre at 19.95° C.<sup>7</sup> or  $0.51 \times 10^{-5}$  gram-molecule per litre at 18° C.<sup>8</sup>; whilst, according to Böttger and Pollatz,<sup>9</sup> the solubility at 25° C. is 0.0025 gram per litre by direct weighing, and 0.0018 gram per litre, estimated by means of conductivity.

The basic salt  $3\text{PbC}_2\text{O}_4 \cdot 7\text{PbO} \cdot \text{H}_2\text{O}$  (?)<sup>10</sup> is formed by the inter-

<sup>1</sup> Sakabi, *Mem Coll Sci., Kyoto*, 1911, 1, 57.

<sup>2</sup> Fox, *Trans Chem Soc.*, 1909, 95, 878.

<sup>3</sup> Rammelsberg, *Pogg. Annalen*, 1853, 90, 28.

<sup>4</sup> Carnus, *Annalen*, 1863, 125, 87. White, *Amer Chem J.*, 1906, 35, 217; White and Nelson, *Amer. Chem J.*, 1906, 35, 227. Wight, *Amer Chem J.*, 1904, 31, 1.

<sup>5</sup> Hutchinson, *Trans Chem. Soc.*, 1893, 63, 1136. Hutchinson and Pollard, *Trans. Chem. Soc.*, 1896, 69, 212; Colson, *Compt rend*, 1903, 136, 675, 891, 1664.

<sup>6</sup> Maumené, *Bull Soc chim*, 1870, 13, 194.

<sup>7</sup> Böttger, *Zeitsch physikal. Chem*, 1903, 46, 602.

<sup>8</sup> Kohlrausch, *Zeitsch physikal. Chem.*, 1908, 64, 159.

<sup>9</sup> Böttger and Pollatz, *Pharm. Post*, 1907, 40, 679.

<sup>10</sup> Strömholm, *Zeitsch. anorg. Chem.*, 1904, 38, 429.

action of lead hydroxide and a soluble oxalate, or by the action of caustic soda on the normal oxalate.

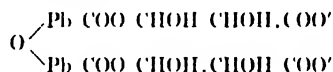
The preparation of  $\text{PbC}_2\text{O}_4 \cdot 2\text{PbO}$  has also been recorded.<sup>1</sup>

The complex salt  $2\text{PbC}_2\text{O}_4 \cdot 2\text{K}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ <sup>2</sup> is formed by acting on lead oxalate with potassium oxalate solution.

**Lead Tartrate**,  $\text{PbC}_4\text{H}_4\text{O}_6$ , is a crystalline powder, obtained by precipitating a lead salt with tartaric acid. It is slightly soluble in water and less soluble in alcohol, as the following figures show<sup>3</sup>:

	Water		Alcohol	
	18° C.	25° C.	18° C.	25° C.
Grams $\text{PbC}_4\text{H}_4\text{O}_6$ in 100 grams solvent	0.0100	0.0108	0.0028	0.0032

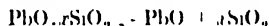
Lead tartrate dissolves in tartaric acid, in alkalis and ammonium salts, with the formation of complex ions. Lead oxide also, like copper oxide and other metallic oxides, dissolves in alkali tartrate solution, producing an alkali salt of plumbotartaric acid, to whose ion the following constitution is attributed<sup>4</sup>:



## LEAD AND SILICON

Silicon is not miscible with lead to an appreciable extent in the liquid state.<sup>5</sup>

**Lead Silicates.**—When litharge is fused with silica it forms a yellow, vitreous silicate which enters into the composition of the lead glazes used in pottery, and also of flint glass, which, on account of its high refractive power, is employed for optical purposes and for making artificial gems. The solubility of lead oxide in lead glass increases with temperature, and the yellow colour of glass rich in lead is attributed to the thermolytic dissociation of lead silicate, thus<sup>6</sup>:



According to Mostowitsch,<sup>7</sup> a number of lead silicates exist, in which the proportion of lead oxide to silica rises from  $\text{PbO} : \text{SiO}_2$  to  $6\text{PbO} : \text{SiO}_2$ .

By the study of the freezing-point curves of mixtures of lead oxide and silica, Hilpert and Weiller<sup>8</sup> find evidence for the existence of only  $\text{PbO} \cdot \text{SiO}_2$ , and probably  $2\text{PbO} \cdot 3\text{SiO}_2$ . According to Hilpert and Nacken,<sup>9</sup> however,  $3\text{PbO} \cdot 2\text{SiO}_2$  exists and probably  $3\text{PbO} \cdot \text{SiO}_2$ .

<sup>1</sup> Pelouze, *Ann. Chem.*, 1842, 42, 268.

<sup>2</sup> Reis, *Ber.*, 1881, 14, 1174.

<sup>3</sup> Partheil and Hubner, *Arch. Pharm.*, 1903, 241, 412, see also Cantoni and Zachoder, *Bull. Soc. chim.*, 1905, [m], 33, 747.

<sup>4</sup> Kahlenberg, *Zeitsch. physikal. Chem.*, 1895, 17, 577, Kahlentz and Hillger, *Chem. Zentr.*, 1897, ii, 399.

<sup>5</sup> Tamaru, *Zeitsch. anorg. Chem.*, 1909, 61, 40.

<sup>6</sup> Bock, *Zeitsch. angew. Chem.*, 1908, 21, 1351.

<sup>7</sup> Mostowitsch, *Metallurgie*, 1907, 4, 647.

<sup>8</sup> Hilpert and Weiller, *Ber.*, 1909, 42, 2969, see also Weiller, *Chem. Zeit.*, 1911, 35, 1063.

<sup>9</sup> Hilpert and Nacken, *Ber.*, 1910, 43, 2565.



Cooper, Shaw, and Loomis,<sup>1</sup> from a study of heating curves, show the existence of  $\text{Pb}_2\text{SiO}_4$ , melting at  $746^\circ \text{C.}$ , as well as  $\text{PbSiO}_3$ , melting at  $766^\circ \text{C.}$

Lead silicates are of importance in pottery manufacture, because, being less soluble than "raw lead" in dilute acid such as occurs in the gastric juice, they are less harmful to the workers. Thorpe and Simmonds<sup>2</sup> have examined the solubilities of various lead silicates in dilute hydrochloric acid, and find that when the molecular proportion of acidic to basic oxide falls below 2 : 1 the silicate is readily attacked by the dilute acid; but when larger proportions of silica are combined with lead oxide there is little action. This is in harmony with the observation of Faraday<sup>3</sup> that glass made of equal weights of silica and lead oxide does not become dull when exposed to the action of hydrogen sulphide; but that a glass made by fusing 8 parts of this glass with 1 part of potash is so tarnished. In the former case the ratio  $\frac{\text{acidic molecules}}{\text{basic molecules}}$  is 3.7, in the latter about 2. It is well known, not only that lead glass is easily fusible, but that it is easily reduced and blackened in the inner blowpipe flame. To account for this reducibility, Simmonds,<sup>4</sup> who recognises the four simple silicates  $\text{Pb}_2\text{SiO}_4$ ,  $\text{PbSiO}_3$ ,  $\text{Pb}_2\text{Si}_3\text{O}_{10}$ , and  $\text{PbSi}_2\text{O}_5$ , as well as various double or complex silicates, introduces certain novel constitutional formula for these compounds, containing oxygen chains and linked silicon atoms.

In a further communication,<sup>5</sup> Simmonds claims that the blackening of lead glass when heated in a reducing flame or a current of hydrogen is due not to the separation of metallic lead, but to the formation of a reduced silicate or "silente" of lead. It was found, indeed, that powdered flint glass, reduced in hydrogen, contained no uncombined lead.

## LEAD AND BORON

**Lead Borates.**—Lead orthoborate is unknown, but the metaborate exists and several poly- or anhydro-borates.

Lead metaborate,  $\text{Pb}(\text{BO}_2)_2 \cdot 11\text{H}_2\text{O}$ , is formed as a white precipitate when cold concentrated solutions of lead nitrate and borax are mixed.<sup>6</sup> It is almost insoluble in, but somewhat hydrolysed by, water, and dissolves readily in dilute acids.

The polyborate  $2\text{PbO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  is obtained by precipitating a solution of a lead salt with excess of boiling borax solution,<sup>7</sup> and  $\text{PbO} \cdot 2\text{B}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$  by treating either of the former salts with a boiling solution of boric acid. Lastly,  $\text{PbO} \cdot 3\text{B}_2\text{O}_3$  is obtained by fusing lead carbonate with boric acid, and extracting excess of the latter with cold water.<sup>8</sup>

<sup>1</sup> Cooper, Shaw, and Loomis, *Ber.*, 1909, 42, 3991, see also *Amer. Chem. J.*, 1912, 47, 273; and *Centr. Min.*, 1912, 289.

<sup>2</sup> Thorpe and Simmonds, *Trans. Chem. Soc.*, 1901, 79, 791, also 1910, 97, 2282.

<sup>3</sup> Faraday, 'On the Manufacture of Optical Glass,' *Phil. Trans.*, 1820, 1.

<sup>4</sup> Simmonds, *Trans. Chem. Soc.*, 1903, 83, 1449.

<sup>5</sup> Simmonds, *Trans. Chem. Soc.*, 1904, 85, 681.

<sup>6</sup> Rose, *Pogg. Annalen*, 1833, 29, 455.

<sup>7</sup> Soubeiran, *J. Pharm. chim.*, 1825, 11, 31.

<sup>8</sup> Le Chatelier, *Bull. Soc. chim.* 1899, [iii], 21, 35.

## LEAD AND CHROMIUM

Lead forms the normal chromate  $\text{PbCrO}_4$ , the dichromate  $\text{PbCr}_2\text{O}_7$ , and several basic salts.

**Normal Lead Chromate**,  $\text{PbCrO}_4$ , occurs naturally as *crocoite* in Siberia, Hungary, Brazil, and other parts; the mineral crystallises in yellow, translucent, monoclinic prisms, and has a density of about 6.0. It was prepared artificially by Bourgeois<sup>1</sup> by heating precipitated lead chromate with dilute nitric acid in sealed tubes at 130° C. The salt is prepared artificially as a bright yellow precipitate by mixing solutions of a lead salt and potassium chromate or dichromate. Probably the precipitate is at first amorphous, but it gradually becomes crystalline. Crystals of lead chromate are also obtained by exposing to the air a solution of the precipitated chromate in caustic soda, by fusing together lead chloride and potassium chromate, by allowing solutions of lead acetate and potassium chromate to mix slowly by diffusion,<sup>2</sup> and by electrolysing a dilute solution of chromic acid with lead electrodes.<sup>3</sup>

Precipitated lead chromate tends to change colour during filtration, becoming orange. This is due to the formation of the red basic salt  $\text{Pb}_2\text{CrO}_5$  or  $\text{PbCrO}_4 \cdot \text{PbO}$  by hydrolysis, which is the more likely to take place when the salt is prepared from basic lead acetate.<sup>4</sup>

Lead chromate is valued as a pigment under the name of *chrome yellow*, *Paris yellow*, or *Leipzig yellow*; and consequently it is important to realise the best conditions for its preparation. It has been shown by Free<sup>5</sup> that the rapid mixing of cold, concentrated solutions of the reacting salts under conditions which prevent the formation of basic salt, produces a crystalline chrome yellow of clear colour and good covering power. Commercial chrome yellow frequently contains lead sulphate, and a pigment known as *Cologne yellow* is prepared by heating lead sulphate with a solution of potassium dichromate. It is recognised that the admixture of lead sulphate to the extent of about 10 per cent. produces a lighter shade, and this is due not only to a physical cause, but to the fact that the presence of a soluble lead salt reduces or prevents hydrolysis, which by producing the basic chromate would cause darkening of colour.<sup>4</sup>

The solubility of lead chromate in water is exceedingly small; indeed, the chromate is probably the least soluble salt of lead. It is practically insoluble also in dilute acetic acid; consequently chromate ions in presence of acetic acid constitute a very delicate test for lead ions in solution. The solubility of lead chromate in water at 25° C. is about  $10^{-4}$  gram per litre according to Kohlrausch,<sup>6</sup> but von Hevesy and Paneth<sup>7</sup> obtained the value  $1.2 \times 10^{-2}$  gram per litre by employing radium-D as a *radioactive indicator*, i.e. by mixing with the lead salt radium-D, which is indistinguishable from lead, and estimating the

<sup>1</sup> Bourgeois, *Bull. Soc. Min.*, 1887, 10, 187.

<sup>2</sup> Dieckmann, *Annalen*, 1873, 87, 121.

<sup>3</sup> Le Blanc and Bindscheller, *Zeitsch. Elektrochem.*, 1902, 8, 255.

<sup>4</sup> Jablczynski, *Chem. Ind.*, 1908, 31, 731.

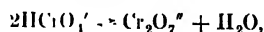
<sup>5</sup> Free, *J. Physical Chem.*, 1909, 13, 114.

<sup>6</sup> Kohlrausch, *Zeitsch. physikal. Chem.*, 1908, 64, 159.

<sup>7</sup> Von Hevesy and Paneth, *Zetsch. anorg. Chem.*, 1913, 82, 323.

radioactivity of the solution, since the original ratio between the two salts is maintained in solution.

Lead chromate readily dissolves in dilute hydrochloric and nitric acids. The solubility of this salt in dilute hydrochloric acid, and the equilibrium between chromate and dichromate in solution, have been studied by Beck and Stegmüller,<sup>1</sup> who find that the solubility in dilute solutions is nearly proportional to the hydrogen ion concentration, but in more concentrated solutions to the square of this concentration. This is on account of the formation of dichromate ions, thus :



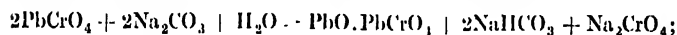
which results in more lead chromate being dissolved.

The following equilibrium constants have been calculated :

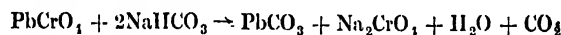
$$\frac{[\text{H}] \cdot [\text{CrO}_4']}{[\text{HCrO}_4']} = 3.7 \times 10^{-7}; \quad \frac{[\text{H}]^2 \cdot [\text{CrO}_4']^2}{[\text{Cr}_2\text{O}_7'']} = 3.4 \times 10^{-13};$$

$$\frac{[\text{H}] \cdot [\text{Cr}_2\text{O}_7'']}{[\text{HCr}_2\text{O}_7']} = 1.0 \times 10^{-3}, \quad \frac{[\text{HCrO}_4']^2}{[\text{Cr}_2\text{O}_7'']} = 2.5.$$

Lead chromate also dissolves in sodium hydroxide solution, being decomposed into a mixture of sodium chromate and plumbite. A solution of sodium carbonate reacts with lead chromate thus :



in presence of excess of sodium hydrogen carbonate, however, the following reaction takes place<sup>2</sup>:



Boiling with potassium nitrate solution causes lead chromate to pass into a colloidal state.<sup>3</sup>

Besides its use as a pigment lead chromate is employed for dyeing or printing on calico. The process, which is a mechanical one, is carried out by passing the fabric first through a solution of lead salt and then through a solution of chromate. The material may, however, be agitated with precipitated lead chromate, suspended in water, alcohol, or benzene. When the two latter media are employed the colour is not so deep as when water is used.<sup>4</sup>

Lead chromate fuses when strongly heated, forming a brown liquid, which on cooling solidifies to a light brown crystalline mass. At a high temperature the salt evolves oxygen, and, on account of its oxidising property, it is employed in organic analysis to aid the combustion of substances containing the elements chlorine and sulphur, which are retained by the lead.

**Lead Dichromate.**  $\text{PbCr}_2\text{O}_7$ , containing 2 molecules of water of crystallisation, was obtained by Preis and Rayman,<sup>5</sup> but its existence was subsequently denied by Autenrieth.<sup>6</sup> Elbs and Nubling<sup>7</sup> found

<sup>1</sup> Beck and Stegmüller, *Arbeiten Kaiserl. Gesundheitsamts*, 1910, 34, 446.

<sup>2</sup> Auerbach and Pock, *Arbeiten Kaiserl. Gesundheitsamts*, 1913, 45, 166.

<sup>3</sup> O. de Coninck, *Bull. Acad. roy. Belg.*, 1909, 665.

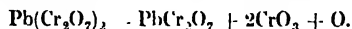
<sup>4</sup> L. Vignon, *Compt. rend.*, 1900, 148, 1329; *Bull. Soc. chim.*, 1900, [iv], 5, 676.

<sup>5</sup> Preis and Rayman, *Ber.*, 1880, 13, 340.

<sup>6</sup> Autenrieth, *Ber.*, 1902, 35, 2057.

<sup>7</sup> Elbs and Nubling, *Zeitsch. Elektrochem.*, 1903, 9, 776.

that when a very concentrated solution of chromic acid (180 grams  $\text{CrO}_3$  per 100 c.c.) is electrolysed with a lead anode a solution is obtained which evolves oxygen when kept, and deposits reddish brown needles of lead dichromate,  $\text{PbCr}_2\text{O}_7$ . From the volume of oxygen evolved it appears that plumbic dichromate is formed and decomposes thus :



Mayer<sup>1</sup> obtained lead dichromate by heating lead acetate with chromic anhydride and concentrated nitric acid, under a reflux condenser; and Cox<sup>2</sup> prepared the same salt by taking account of the fact that it is prone to hydrolysis and can only be formed in contact with a chromic acid solution of a certain concentration, which is 6.865 gram-molecules  $\text{CrO}_3$  per litre at 25° C. Thus by grinding together lead monoxide and chromium trioxide in saturated solution in the proportion of 2 gram-molecules of the former to 5 of the latter, lead dichromate is produced and may be obtained pure after washing with 7-N solution of  $\text{CrO}_3$ . It is a lustrous, red, crystalline powder.

**Basic Lead Chromate**,  $\text{Pb}_2\text{CrO}_5$ ,  $\text{PbCrO}_4 \cdot \text{PbO}$ , or  $2\text{PbO} \cdot \text{CrO}_3$ , is formed as a red powder by the action of cold caustic soda solution on the normal chromate. It is also produced by mixing together lead chromate and oxide in presence of water, and is known commercially by various names: *chrome red*, *orange chrome*, *Derby red*, *Chinese red*, according to its depth of colour. It is converted by acetic acid into the normal salt, and the two salts are in equilibrium<sup>3</sup> in contact with an aqueous solution of  $2 \times 10^{-5}$  molecules  $\text{CrO}_3$  per litre at 25° C. Mixtures of the two salts produce shades intermediate between yellow and red: such mixtures are known commercially.

The basic salt  $\text{Pb}_2\text{Cr}_2\text{O}_6$  occurs in dark red hexagonal prisms of a density of 5.75 as the mineral *plumbite* or *plumbocrocoite*. This compound may be prepared artificially by allowing solutions of lead nitrate and potassium chromate to mix by diffusion,<sup>4</sup> by exposing a solution of lead chromate in caustic potash to the air for several months,<sup>4</sup> or by immersing galena in potassium dichromate solution for six months. This last process, which was carried out by Mounier,<sup>5</sup> probably nearly reproduces the conditions by which the mineral is naturally produced.

**Lead Chromate Double Salts** - Double salts of lead chromate with alkali chromates have been obtained.<sup>6</sup> The potassium salt  $\text{K}_2\text{CrO}_4 \cdot \text{PbCrO}_4$  or  $\text{K}_2\text{Pb}(\text{CrO}_4)_2$  is formed as a yellow amorphous precipitate when 50 c.c. of a saturated solution of potassium chromate is mixed with 10 c.c. of saturated lead acetate solution. The ammonium salt  $(\text{NH}_4)_2\text{Pb}(\text{CrO}_4)_2$  is prepared similarly, and both salts are decomposed into their components by water.

<sup>1</sup> Mayer, *Ber.*, 1903, 36, 1740.

<sup>2</sup> Cox, *Zentralb. anorg. Chem.*, 1906, 50, 226.

<sup>3</sup> Drevermann, *Annalen*, 1853, 87, 121.

<sup>4</sup> Ludeking, *Amer. J. Sci.*, 1892, [iii] 44, 57.

<sup>5</sup> Mounier, *Compt. rend.*, 1878, 87, 674.

<sup>6</sup> Gröger, *Zeitsch. anorg. Chem.*, 1907, 54, 185; 1908, 58, 112; Batté, *Compt. rend.*, 1914, 158, 495.

## LEAD AND MOLYBDENUM

**Lead Molybdate**,  $\text{PbMoO}_4$ , occurs as the mineral *wulfenite*, which was prepared artificially by Mauross<sup>1</sup> by fusing together lead chloride and sodium molybdate, and was so obtained in yellow hexagonal tablets. This salt is quantitatively precipitated<sup>2</sup> as a white powder by mixing sodium molybdate and lead nitrate solutions. After fusion at high temperature it crystallises, and then has a density<sup>3</sup> of 6.62.

## LEAD AND TUNGSTEN

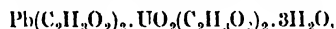
**Lead Tungstate**,  $\text{PbWO}_4$ , occurs as the mineral *stolzite*, which was also obtained by Mauross<sup>1</sup> by fusing lead chloride with sodium tungstate. The same salt is formed as a white precipitate when solutions of a lead salt and potassium tungstate,  $\text{K}_2\text{WO}_4$ , are mixed.

**Lead Metatungstate**,  $\text{PbW}_{12}\text{O}_{42} \cdot 5\text{H}_2\text{O}$ , is produced as a flocculent precipitate when a solution of metatungstic acid or its soluble salt is added to lead acetate solution.

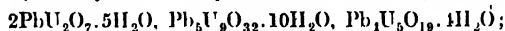
## LEAD AND URANIUM

**Lead Diuranate**,  $\text{PbU}_2\text{O}_7$ , is said to be formed<sup>4</sup> when uranyl acetate solution is digested with freshly precipitated lead carbonate; when ammonia<sup>5</sup> is added to a mixture of uranyl and lead nitrate solutions, and when lead acetate and uranyl nitrate solutions are mixed together. It is described as a yellowish red precipitate, soluble in acetic acid, which turns brown on heating, and when reduced in hydrogen yields pyrophoric lead and uranous oxide,  $\text{UO}_2$ .

The following salts have been obtained by Zehnter<sup>6</sup>.



which on ignition yields  $\text{PbUO}_4$  as a reddish brown crystalline mass;



also  $[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_3 \cdot 2\text{H}_2\text{O}]3\text{H}_2\text{O}$ , which yields  $\text{PbU}_4\text{O}_{10}$  on ignition.

**Lead Peruranate**,<sup>7</sup> combined with lead uranate as the salt  $(\text{PbO})_2\text{UO}_4 \cdot \text{PbUO}_4$ , is formed as an orange precipitate when solutions of sodium peruranate,  $(\text{Na}_2\text{O}_2)_2\text{UO}_4$ , and lead acetate are mixed. With dilute sulphuric acid this salt yields hydrogen peroxide, and with the concentrated acid ozonised oxygen; whilst dilute acetic acid decomposes it, forming lead acetate and uranium tetroxide,  $\text{UO}_4$ .

## DETECTION AND ESTIMATION OF LEAD

It was early observed that the presence of lead in wine could be detected by the addition of sulphuric acid; and Zeller in 1707 suggested

<sup>1</sup> Mauross, *Annalen*, 1852, 82, 358.

<sup>2</sup> Chatard, *Ber*, 1871, 4, 280.

<sup>3</sup> Cozza, *Compt. rend*, 1885, 102, 1315.

<sup>4</sup> Wetherill, *J. prakt. Chem.*, 1843, [1], 29, 207.

<sup>5</sup> Arfwedson, *Pogg. Annalen*, 1821, 1, 258.

<sup>6</sup> Zehnter, *Monatsh*, 1904, 25, 197.

<sup>7</sup> Melnikoff and Pissajewski, *Ber*, 1897, 30, 2902.

an extract of orpiment and lime-water, which would contain sulphide, as a test for lead salts, which it turned black. The introduction of hydrogen sulphide as an analytical reagent was first made in connection with lead salts; for Fourcroy and Hahnemann in 1787 proposed to use water acidified with hydrochloric acid and saturated with hydrogen sulphide as a test for lead.

**Detection in the Dry Way.** Lead salts impart a bluish grey tint to the Bunsen flame, which does not, however, show a clearly defined spectrum. The spark spectrum of lead contains characteristic lines in the orange, green, and violet (see p. 374). Owing to the easy reducibility of lead oxide, lead salts yield a bead of the metal when heated with sodium carbonate on charcoal before the blowpipe. The metal is identified by its malleability, by the fact that it marks paper, and by dissolving it in nitric acid and applying to the solution one or other of the characteristic wet tests.

**Detection by Reactions in Solution.** From moderately concentrated solutions lead is precipitated as chloride by hydrochloric acid, and this reaction is employed to separate lead, together with silver, and mercurous mercury in qualitative analysis.

Lead remaining in solution after the addition of hydrochloric acid is detected and separated by means of hydrogen sulphide, with which it yields a black precipitate of the sulphide. Copper, mercury, and bismuth also give black or dark brown precipitates with the same reagent, but the lead is separated and identified by the solubility of its sulphide in moderately concentrated nitric acid and the subsequent precipitation of the sulphate by dilute sulphuric acid. The lead sulphate may then be dissolved in ammonium acetate solution, and the lead precipitated as chromate.

The sulphide and chromate tests are both very delicate, and may be employed for the detection of lead in potable water. The sulphide test is generally employed in presence of a little dilute hydrochloric acid, though it is even more delicate in presence of alkali. In either case the absence of other metals which might give brown colorations or black precipitates must be ascertained. The chromate test is carried out in presence of dilute acetic acid. Other and less important tests for lead are as follow: Alkalis precipitate lead hydroxide, soluble in excess of the precipitant, but insoluble in ammonia; alkali carbonate precipitates basic lead carbonate, insoluble in excess; alkali iodide precipitates yellow lead iodide, soluble in hot water from which it crystallises in golden spangles; metallic zinc separates lead in crystals, forming the lead tree.

A reagent for detecting traces of lead and manganese exists in the form of tetramethyldiaminodiphenylmethane, which gives a deep blue colour with lead and manganese dioxides. The substance to be tested is incinerated with sulphuric acid; a few drops of sodium hypochlorite solution are added to the ash, excess of chlorine is eliminated by heating, and the reagent is added. By the blue colour produced lead has been detected in water which has passed through lead pipes, or in an animal body, when other methods have failed.

**Estimation of Lead.**—Lead may be estimated by three series of methods: (i) gravimetric, (ii) volumetric, (iii) electrolytic.

(i) *Gravimetric Methods.* (a) Lead is precipitated from solution as sulphate by dilute sulphuric acid, a volume of alcohol equal to twice

the volume of the solution being added to secure complete precipitation. The precipitate is then filtered off through a weighed filter, or preferably a Gooch crucible, dried, and weighed.

(b) Lead may also be precipitated as basic carbonate or oxalate, and these are converted by ignition into monoxide, which is weighed.

(c) Lead is occasionally weighed as chloride, chromate,<sup>1</sup> molybdate,<sup>2</sup> or oxalate.

(iii) *Volumetric Methods.*—(a) The method of Alexander consists in titrating an ammonium acetate solution of lead sulphate with ammonium molybdate solution which has been standardised with a similar lead solution of known strength. The end point is found by a spot reaction with a solution of tannin which gives a yellow colour with molybdate.

(b) Lead may also be estimated by precipitating with excess of standard chromate solution, filtering and washing the precipitate, and estimating the excess of chromate by adding acidified potassium iodide, and titrating the liberated iodine with thiosulphate.<sup>3</sup>

It is possible also to titrate a hot solution of a lead salt by standard chromate, employing the shaking method.<sup>4</sup>

(c) A further method of estimating lead consists in obtaining it as sulphate, dissolving this in ammonium acetate, and oxidising to dioxide by bromine water, the dioxide being then estimated iodometrically.<sup>5</sup>

(d) After lead has been converted into sulphate it may be estimated volumetrically by decomposing this salt with hydrogen sulphide, and titrating the liberated sulphuric acid.<sup>6</sup>

(e) Traces of lead are estimated colorimetrically by means of hydrogen sulphide, the depth of colour produced being matched by means of a standard lead solution. By this method 0.05 mg. of lead per litre can be estimated.<sup>7</sup>

(iii) *Electrolytic Methods.*—Lead has usually been estimated electrolytically by separation from nitric acid solution, as lead peroxide at the anode. From a faintly acid, ammoniacal or alkaline solution, however, it can be separated as metal at the cathode. Classen<sup>8</sup> has found that with a current density of 1.5 to 1.7 amperes per square decim. the separation of lead as lead dioxide is complete in four to five hours at a temperature of 10° to 50° C. The lead dioxide is then washed and dried at 180° C. The special precautions necessary for this estimation have been studied by Vortmann.<sup>9</sup>

The introduction of rotating electrodes has enabled electro-analysis to be carried out very rapidly; and the estimation of lead by this means, as well as the separation of various metals by the use of graded potential, has been successfully accomplished by Sand.<sup>10</sup>

<sup>1</sup> Pollot, *Bull. Soc. chim.*, 1876, [iv], 26, 248.

<sup>2</sup> Smith and Bradbury, *Ber.*, 1891, 24, 2930.

<sup>3</sup> Diehl, *Zeitsch. anal. Chem.*, 1880, 19, 306.

<sup>4</sup> Lewis, *Dissertation*, Breslau, 1908.

<sup>5</sup> Kuhn, *Arbeiten Kaiserl. Gesundheitsamte*, 1906, 23, 389.

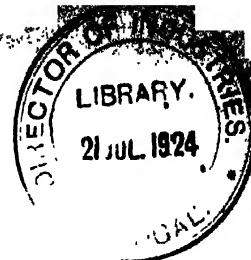
<sup>6</sup> Miles, *Trans. Chem. Soc.*, 1915, 107, 988.

<sup>7</sup> Woudstra, *Zeitsch. anorg. Chem.*, 1908, 58, 168; see also Harcourt, *Trans. Chem. Soc.*, 1910, 97, 841.

<sup>8</sup> Classen, *Ber.*, 1891, 27, 163.

<sup>9</sup> Vortmann, *Annalen*, 1907, 351, 283.

<sup>10</sup> Sand, *Trans. Chem. Soc.*, 1907, 91, 373.



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